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THE INSTITUTE OF PETROLEUM

AN Ordinary General Meeting of the Institute of Petroleum was held at 61 New Cavendish Street, London, W.1, on 7 May 1958, the Chair being taken by Dr E. B. Evans, a member of Council.

The minutes of the previous meeting were confirmed and signed as a correct record. The names of members elected since the previous meeting were announced.

The Chairman introduced the author, and the following paper was presented in summary.

RECENT DEVELOPMENTS IN REFINING *

By W. J. NEWBY †

SUMMARY

From 1952 onwards substantially all the emphasis in the oil industry has been on motor gasoline quality. This has been necessary to keep pace with the demands of the automotive industry. Compression ratios of internal combustion engines have increased significantly and there has been a parallel demand for increases in motor gasoline O.N. Substantial process developments have been necessary to meet this demand, including the commercial introduction of catalytic reforming and its development into a key process for octane improvement. The introduction of this process has made available large quantities of hydrogen and a variety of versatile processes have been developed using catalytic reformer hydrogen for desulphurizing or otherwise improving the quality of a wide range of petroleum products. The more important developments in these two fields are discussed within the context of Western European requirements.

MOTOR GASOLINES

SIGNIFICANT increases in compression ratios by the designers of internal combustion engines began in the U.S.A. in 1952–53. These have continued at a rate of just under 0·5 numbers per year. Over the same period research O.N. of motor gasolines increased by between 1·0 and 1·5 numbers per year. This rate of octane improvement would not have been possible but for the rapid commercial development of catalytic reforming.

Catalytic reforming is a process for the conversion of low O.N. naphthas to high O.N. gasolines. Octane gains of some 40 to 60 numbers are possible in yields ranging from 70 to 90 per cent according to the nature of feedstock and the severity of operation. The octane improvement is achieved principally by the conversion of naphthenes, and to a lesser extent paraffins, to aromatics. Aromatics in the gasoline boiling range have leaded O.N. of over 100. This process has thus opened up a vast new source of octane potential from materials previously considered relatively unsuitable for motor gasoline. The rapid development of this source of additional O.N., more than any other factor, has set the pace for the present trends in engine design. The extent of these developments is illustrated by the representative U.S. data shown in Table I.

To what extent these trends will continue in the future is not known. Nor is it apparent how far O.N. can be raised before economic considerations become over-riding, or to what compression ratios engines can be increased before mechanical considerations become limiting. However, for the immediate future it is the general consensus of opinion that present improvements in engine design will continue and the demand for regular increases in O.N. will persist.

TABLE I

U.S. Gasoline and Engine Data

	Compression ratio		Gasoline octane number		Catalytic reforming installed capacity 1000 b.p.s.d.
	Average	Highest	Regular	Premium	
1946	6·75	7·25	80	86	Nil
1952	7·0	8·0	84	91	Nominal
1954	7·25	8·5	87	94	250
1956	8·5	9·5	89	96	900
1958	9·5	10·5	92	99	1,250

Motor gasolines are currently marketed at approximately the following research octane levels:

	Premium	Regular	Pool
U.S.A. (2·5 ml TEL/USG)	99	92	96
Europe (1·8 ml TEL/IG)	96	86	90

Only a very small proportion of the world's car population requires gasolines of 100 research O.N. and higher, but some refiners, particularly in the U.S.A., the U.K., and Italy, market a small quantity of a third grade at levels of 100 and over to meet the demands of the highest requirement cars. At present levels of regular, premium, and super premium production, existing conventional processes, such as thermal reforming and cracking, catalytic cracking, polymerization, and catalytic reforming, are adequate.

* MS received 17 March 1958.

† The British Petroleum Co. Ltd.

It is not expected that O.N. will increase more rapidly than during the last few years, and for the immediate future most European refineries can be modernized by stepping up the severity of existing processes. So far refiners have been able to keep pace with the engine designers mainly by increasing the capacity and severity of catalytic reforming. By the next stage of upgrading, feedstocks for this process will have become exhausted and further gains will be achieved only by the installation of new processes or by substantial modifications to existing processes. It is against this background that recent developments should be viewed.

GAINING OCTANE NUMBER

Numerous new ways of gaining O.N. have been developed, mainly in the U.S.A. These, in conjunction with catalytic cracking, are suitable for stepwise installation for the production of gasoline pools of the order of 100 research O.N. The various steps available include high severity catalytic reforming, reformate splitting, alkylation, and isomerization of light straight-run gasoline. For the production of ceiling grades the extraction of pure aromatics from reformates is envisaged. These developments are ideally suited for refineries designed for maximum motor gasoline and in which catalytic cracking provides a substantial proportion of the high octane material.

They are not wholly applicable to the situation existing in Western Europe because the ratio between gasoline and fuel requirements is such that catalytic cracking must be kept to a minimum. A comparison between the requirements for the two areas is shown in Table II.

TABLE II

Western Europe and U.S.A. Product Requirements

	Western Europe	U.S.A.
Gasolines	20	45
Kerosines	4	4
Gas/diesel	23	23
Residual fuel	36	14

The over-riding effect this has is shown in Table III, in which the O.N. of pooled gasolines for various combinations of processes are given in a number of theoretical refineries operating on Kuwait crude. Kuwait crude has been chosen as being representative of a Middle East crude. The octane potential is markedly higher for the refineries equipped with catalytic cracking. The yields of gasolines in these cases, however, are in excess of requirements for Western Europe. Unless there is a major shift in the relative requirements for gasoline and fuel, it is unlikely that additional catalytic cracking capacity will be installed in future expansions, and the general feature of modern refinery design tends towards the production of motor gasolines from the gasoline, benzene, and naphtha fractions of crude only. This restricts the choice of methods for octane improvement and makes the problem of upgrading a relatively difficult one.

TABLE III

Theoretical Refineries Operating on Kuwait Crude

	Motor Gasoline, % vol.	Octane number, +1·5 ml TEL/IG	Middle Distillate % vol.	Bunker C, % vol.
No catalytic cracker				
Distillation	23·1	65	26·3	49·5
Distillation + cat reforming	17·6	91	26·3	49·5
Distillation + cat reforming + isomerization	17·4	94	26·3	49·5
With catalytic cracker				
Distillation + cat cracking	35·1	78	24·1	34·3
Distillation + cat cracking + cat polymerization	37·7	80	24·1	34·3
Distillation + cat reforming + cat cracking	31·6	94	24·1	34·3
Distillation + cat reforming + cat cracking + cat polymerization	34·2	95	24·1	34·3
Distillation + cat reforming + isomerization + cat cracking	31·4	97	24·1	34·3
Distillation + cat reforming + isomerization + cat cracking + cat polymerization	34·0	98	24·1	34·3

Apart from O.N., motor gasolines have special requirements for volatility. Excess front end volatility must be avoided to prevent vapour lock, and adequate middle volatility must be provided to ensure good performance. These are features which are easily controlled in a complex refinery, where the choice of components is large. In a simple refinery, where a catalytic reformer is the only upgrading equipment, the O.N. of the straight-run gasoline is too low for inclusion in high O.N. premium grades, and with a balanced production of regular and premium gasolines a surplus of light gasoline is produced. The disposal or upgrading of this is of special significance for Western European refineries, and this will become of increasing importance as O.N. are increased.

To ensure the future, therefore, the requirements for Western Europe will be for the highest possible severity in catalytic reforming and for processes which will upgrade light gasoline. In the first instance the extension of thermal processes is the most likely route that will be followed, including thermal reforming of catalytic reformates, thermal reforming or steam cracking of light gasoline, and polymerization of thermal olefins. The combination of these processes, however, will not produce the very high pool O.N. envisaged by recent U.S. publications, and substantial new developments will be necessary to achieve these values if catalytic cracking is kept to a minimum.

In Table IV typical modern data for a number of processes are summarized. It is beyond the scope of this paper to discuss how these products may be blended to produce high O.N. gasolines, but considerable process developments are reflected in these data, and these are discussed in the following sections.

TABLE IV

Motor Gasoline Components—Kuwait Crude

	Research octane numbers			Volatility at 100° C
	Clear	+1·5 ml TEL/IG	+3·6 ml TEL/IG	
Cat cracked gasolines (350°–550° C feed)				
Full range	94	97	98·5	51
Light to 100° C	95	99	101	98
Light to 160° C	94·5	97·5	99	70
Catalytic reformates				
88 O.N. ex 95°–175° C feed	88	95	98	33
92·5 O.N. " " " "	92·5	98	100	35
95 O.N. " " " "	95	99·5	101·5	36
100 O.N. " " " "	100	103	104	33
90 O.N. " 95°–140° C "	90	96	99	48
95 O.N. " " " "	95	99·5	101·5	48
100 O.N. " 70°–130° C "	100	103·5	106	48
Thermal reformates				
Gasoline feed	80	90	95	86
Naphtha feed	83	90	94	32
88 O.N. catalytic reformate	101	104	105	30
Split light cat reformate	95·5	99	100·5	55
Split catalytic reformates				
<100° C ex 95 O.N.	74	87	94	100
>100° C ex 95 O.N.	105	107·5	108·5	Nil
Steam cracked gasolines				
Gasoline feed	90	95	97·5	86
Naphtha feed	97	99	101	26
Commercial isopentane	90	100·5	106	100
Straight-run gasoline	63	76	83	100

GASOLINE PROCESSES

Catalytic Reforming

The U.O.P. Platforming process was announced in 1949 and commercial operation was commenced in 1952. This was the first platinum catalytic reforming process. There are now 11 different processes in commercial use. Seven are based on fixed-bed operation, employing platinum on alumina catalyst, two on moving-bed and two on fluid-bed operation employing molybdenum, cobalt, or chromium oxides on alumina catalysts. The non-platinum processes have not found general acceptance and account for less than 10 per cent of installed capacity. Platforming accounts for over 50 per cent of installed capacity, but as requirements for increased severity of operation have developed the new regenerative processes are beginning to account for a steadily increasing proportion of new plant. Of these Ultraforming, Powerforming, and Sinclair/Baker are prominent.

New developments have been almost entirely towards increased severity of operation. These include feedstock pretreatment with process hydrogen for the reduction of sulphur and the removal of trace materials, which poison the catalyst at high severities, the development of new catalysts, especially of higher platinum contents, and the use of lower space velocities.

The fixed-bed processes are similar in design and employ three or more reactors in series with intermediate reheat facilities and recycle of process hydrogen. The essential difference with the new processes is that the catalysts can be regenerated *in situ* to restore catalyst activity by burning off process carbon. This enables the use of optimum process conditions to achieve maximum upgrading irrespective of the rate of catalyst deactivation. Low space velocities and high catalyst loadings are necessary and frequent regeneration is practised.

The actual octane ceiling for commercial operation with the non-regenerative type of process has not yet been established. In this the nature of the feedstock is an important factor. Naphthas from Middle East crudes are normally regarded as being relatively poor because of their low naphthene content. However, over the last few years much new experience has been gained with Middle East feedstocks, and this indicates that long periods of commercial operation are possible at high severities without the need for frequent regeneration. An example of this type of commercial operation is given in Table V. These results were obtained in a Platformer originally designed for a severity of 88 O.N. clear.

TABLE V

High Severity Catalytic Reforming at Kent Refinery

Feed	
Composition:	
Paraffins % wt	64
Naphthenes % wt	23
Aromatics % wt	13
ASTM	
Distillation, ° C	100–175
Charge rate, b.p.s.d.	5,320
Total, brl	1,073,900
Product	
O.N., research	95
Engler % vol at 100° C	38
Make, brl	787,200
Yield, % wt	75·4
R8 catalyst (*U.O.P.*)	
Charge, lb	26,190
On stream, days	247
Life at 95 O.N. brl/lb	41
overall brl/lb	46

Catalytic Reforming Combination Processes

Catalytic reformates are essentially mixtures of paraffins and aromatics with a small residue of unconverted naphthenes. Typical distributions of hydrocarbons are shown in Table VI.

The paraffins are predominantly low in boiling range, and simple distillation is an effective method of splitting catalytic reformates into high and low O.N. components. The high octane fraction is inyolatile, but in blend with light fractions of catalytically-cracked gasoline, thermal reformates, or *iso*paraffins is a key component for the production of high octane gasolines. The material boiling below 100° C is mainly paraffinic, and it is of interest that for a wide range of severities its research O.N. is substantially constant. Typical separations that can be effected by distillation of Middle East reformates

TABLE VI

Hydrocarbon Distribution in Catalytic Reformates from Kuwait Crude

Product	Boiling range, ° C		
C_5 paraffins	32·5–45	8·5	7·8
C_6 paraffins	45–75	16·3	13·7
C_7 paraffins	75–109	12·9	11·9
C_{8+} paraffins	109–EP	10·3	4·1
Total		47·0	37·5
cyclo C_5 and naphthenes	45–EP	2·5	1·5
Benzene		2·3	3·0
Toluene		8·3	11·0
C_8 aromatics		13·2	18·5
C_{9+} aromatics	145–EP	26·7	27·5
Total		50·5	60·0
Research O.N.		88·5	94
Feedstock boiling range, ° C		80–190	90–175

TABLE VII

Splitting of Middle East Reformates

Research O.N.			Yield % wt Residue
Reformate Clear	Overhead + 1·5 ml TEL/IG	Residue + 1·5 ml TEL/IG	
74·0	85·0	84·5	75·5
85·5	86·5	100·0	58·5
85·5	86·0	103·5	36·5
87·0	84·0	103·5	43·0
91·5	84·0	103·5	64·0
91·5	86·0	105·5	46·5
94·0	86·0	105·0	65·5
94·0	88·5	108·5	48·0
95·5	88·0	111·5	56·0

in a simple splitter with low fractionating efficiency are shown in Table VII.

Reformate splitting does not increase the overall O.N., but by thermally reforming splitter overheads or total catalytic reformates substantial upgrading can be achieved. Typical data for this operation are shown in Table IV. Conventional thermal reforming conditions are satisfactory and the product is gum-stable. Catalytic polymerization of the gaseous olefins from this operation may be carried out to increase the overall yield. This method of gaining O.N. is attractive where thermal reforming and catalytic polymerization are already installed and represents a typical example of how conventional equipment can be adapted to keep pace with octane requirements.

Two combination processes have also been developed based on aromatic extraction of catalytic reformate. These are Rexforming, by U.O.P., and Iso-plus, by Houdry. The paraffinic raffinate can be recycled or reprocessed in a separate catalytic reformer or blended into aviation turbine fuels. These processes in effect increase equilibrium aromatic content and foster paraffin dehydrocyclization. Reformate yields and octane ceilings are raised. The processes have not yet, however, found wide acceptance.

Isomerization

All the aromatic compounds in the gasoline boiling range have leaded O.N. of greater than 100, but they are high-boiling and, apart from benzene, contribute nothing to volatility requirements. The only available volatile hydrocarbons of high O.N. are either olefins or *iso*paraffins. Volatile olefins are available from conventional processes such as catalytic cracking and thermal reforming, but in the search for additional O.N., attention has been given to the production of *iso*paraffins. C_5 and C_6 *iso* or branched-chain paraffins have substantially higher O.N. than their respective normal compounds, as shown by the data in Table VIII.

TABLE VIII

Octane Number of Low-boiling Hydrocarbons

Pure hydrocarbons	B.p. ° C	Octane numbers	
		1·2 ml TEL/IG	3·6 ml TEL/IG
Normal pentane	36	75·5	84·7
*iso*Pentane	28	104·2	108·6
Normal hexane	69	43·4	65·3
2-2 Dimethylbutane	50	101·3	106·0
2-3 Dimethylbutane	58	113·1	—
2- Methylpentane	60	84·6	93·1
3- Methylpentane	63	85·0	93·4

Five processes have recently been announced for isomerizing C_5, C_6, or C_5/C_6 mixtures. These are Iso-Kel, by Kellogg, Penex, by U.O.P., Pentaforming, by Atlantic, Isomerate, by Pure Oil, and Isomate, by Standard Oil of Indiana. By recycling, these processes approach thermodynamic equilibrium proportions of *iso*paraffins. Isomerization is achieved catalytically in the presence of hydrogen. The reaction units are relatively simple, but close fractionation is necessary to separate the *iso* and normal paraffins. These processes are limited by thermodynamic equilibria and for the temperatures at which they normally operate are not satisfactory without some degree of super-fractionation to remove low O.N. normal paraffins. In most European situations, however, there is normally sufficient *iso*pentane in the crude to meet premium gasoline requirements, and it is unlikely that isomerization will find ready application in this hemisphere in the immediate future, particularly also as the lower level of TEL

content does not permit full advantage of the *iso*-paraffins to be taken.

Catalytic Cracking

Progress in both fluid-bed and moving-bed catalytic cracker design during the last five years has consisted mainly of cheapening the process by reductions in capital and operating costs. No fundamental changes in the principles on which the processes operate have been made. Among the most important of the factors which have received detailed study is the arrangement of the reactor and regenerator to reduce structural steel requirements, improvements in gas distribution, and improvements in catalyst transfer methods.

With fluid-bed operation, designs have emerged in which the structural steel requirements have been reduced considerably by combining the reactor and regenerator in a single, self-supporting column. From an engineering point of view it is easier to superimpose the reactor over the regenerator, since the regenerator has the greater diameter. This is the basis of modern U.O.P. designs. A feature of this design is that a long vapour pipe is required to transfer catalyst and feed to the reactor. Considerable cracking occurs during this transfer so that the catalyst requirement is reduced. The Kellogg "Orthoflow" process reverses the position of the reactor and regenerator. Catalyst transfer lines and the catalyst stripper consist of almost straight pipes constructed within the two vessels. This minimizes changes in direction of the catalyst during transfer and helps to reduce attrition of the catalyst.

New designs of the distribution grids for the reactor and regenerator have resulted in improved coke burning and reaction rates. As a result, carbon contents of spent and regenerated catalyst and the oxygen content of the flue gas have been reduced considerably. Reduction of excess oxygen has made increased regenerator temperatures possible without the risk of afterburn of the carbon monoxide at the regenerator cyclones. The resultant lower carbon levels of the regenerated catalyst have improved catalyst utilization and unit control. In the SOD Model IV design, the control of the catalyst flow is achieved entirely by density and level differences in a unit in which a side-by-side reactor and regenerator arrangement is connected by U-pipes. Transfer line cracking is made a special feature in a Shell two-stage catalytic cracker. Transfer line cracking takes place at high temperatures and with a short contact time. Destruction of gasoline by secondary cracking does not occur at this stage. The primary cracked products are separated and the remaining uncracked material is treated in a conventional reactor. This process is claimed to give increased yields.

Modern designs of TCC and Houdriflow moving-bed plants have adopted air or gas lifts to maintain circulation of the pelleted catalyst rather than elevators employed in earlier designs. These processes have special advantages resulting from the very complete coke removal possible from a relatively slow moving bed in which high reactor and stripping efficiencies are possible. However, the advances that have been made with fluid-bed processes have to some extent reduced the advantages of the moving-bed designs.

The basic catalytic cracking catalyst remains silica alumina, similar in composition to the original Houdry fixed-bed catalyst, but a number of improvements have been made in the manufacture of spray-dried and ground catalysts. By attention to size ranges and particle characteristics, better fluidization and lower stack losses have been achieved. Attention has been given to improving steam and heat stability by modifying physical characteristics such as pore volume and by modifications in catalyst composition. Changes in composition are also reported to change product distribution. Developments in this field are of special interest to Western Europe, particularly if it proves possible to obtain lower gasoline and higher gas oil yields, and the production of low pour point gas oils at the expense of wax distillate and gasoline.

The main catalytic feedstock has continued to be distillate in the boiling range 350°–600° C. The end point is restricted to maintain a low metal content which would otherwise deposit on the catalyst and impair its activity. Two separate processes have been developed which overcome this problem and enable atmospheric residues to be processed satisfactorily. In the decarbonizing process, the feedstock is freed from metals by the removal of asphalt in a propane deasphalting tower. In the Houdresid moving-bed process, the metals which deposit on the catalyst are continuously eliminated by attrition in the catalyst gas lift.

Alkylation and Polymerization

With the continued trend for octane improvement, a demand for high O.N. paraffinic or olefinic components is a complementary requirement to the production of aromatic components from catalytic reforming. Alkylation and polymerization provide such components. A greater yield is given by alkylation than by polymerization for a given quantity of olefins, and alkylate has a lower sensitivity and a higher lead response. This has resulted in an increased use of alkylation for the production of motor fuel in the U.S.A. As in the case of catalytic cracking, advances in alkylation techniques have resulted in cheaper and more economical plants without fundamental changes in the process. Sulphuric and hydrofluoric acids remain by far the most important of the alkylation catalysts. Both are capable of producing high quality alkylate, and the choice between the two catalysts generally depends on the economics of acid supply, recovery, or disposal. Early sulphuric acid

alkylation units consumed 1 to 1·5 lb of acid/USG of alkylate produced. The most notable feature of modern designs is that acid consumption has been reduced to about 0·5 lb/USG of alkylate. Turbo-mixers have replaced jet-mixers, providing more favourable reaction conditions, as well as effecting a considerable reduction in reactor power requirements. The Kellogg sulphuric acid alkylation process employs three to five turbo-mixers, and the acid settler is combined in a single vessel. Auto-refrigeration is employed. The Stratco process, also using sulphuric acid catalyst, has one or two turbo-mixers with a separate acid settler. The reactor effluent is cooled by vaporization of *iso*butane and the chilled effluent is used for reactor cooling by circulation through the coils of the contactor. Both auto-refrigeration and effluent cooling provide recycle *iso*butane to supplement *iso*butane recycle from the de-*iso*butanizer tower and thereby increase the *iso*-butane/butene ratio. The newer plant designs show very large savings in equipment, which has been reduced by as much as 50 per cent. Processes using hydrofluoric acid catalyst are licensed by the Phillips Petroleum Company and U.O.P. Both designs employ turbo-mixers, and refrigeration is not necessary. Acid consumption for these units is about 0·2 lb/brl alkylate.

Catalytic polymerization of C_3/C_4 olefin feedstock to make high octane motor gasoline was one of the earliest catalytic processes in the petroleum industry. The original U.O.P. phosphoric acid on kieselguhr catalyst has retained its place as the leading catalyst in this process. For motor gasoline manufacture a compact and easily-controlled reactor of the water/steam cooled exchanger type has been developed. Polymerization takes place at high pressure, and the catalyst life is about 200–300 USG polymer/lb catalyst. Regeneration of spent catalyst at the end of a run is not economically justified and the spent catalyst is discarded.

Chemical Treatments

During the last five years there has been a growing acceptance of inhibitor treatment for sweetening gasolines. This process is only applicable to cracked stocks, as the mechanism demands the presence of an olefin. Sour gasoline is contacted with a phenylene-diamine inhibitor in the presence of caustic and air. Mercaptans are converted to disulphides. The method of use varies for different stocks. For thermally-cracked materials it is usually sufficient to add inhibitor and allow the sweetening to take place in storage. With catalytic cracker stocks, intimate mixing and attention to temperature is necessary to achieve rapid sweetening. Failure in this respect tends to form peroxides and gums which affect engine cleanliness.

A wide range of satisfactory sweetening processes for converting mercaptans to disulphides exists, but as octane demand has increased, particular attention is being given to the removal of mercaptans in order to reduce sulphur content and improve TEL response. The plumbite process is virtually obsolete for gasolines, but a modified fixed-bed operation known as the Bender Process has been developed for treating kerosines. The hypochlorite process has also largely disappeared, mainly on the grounds of cost. The solutizer processes are finding increased application and are particularly suitable for straight-run Middle East stocks. Light catalytically-cracked gasolines can be conveniently sweetened by solutizer alone. Slurry copper chloride has become the industry's most versatile sweetening process and may be successfully applied to thermally-cracked, catalytically-cracked, and straight-run materials up to the kerosine boiling range. Sulphuric acid treatment still has a place in the industry, being used for the treatment of colour unstable kerosines, sulphur reduction of *iso*pentane, and the preparation of white spirits and special boiling point solvents of good odour. A variety of direct oxidation processes have been developed based on catalysed cresylate solutions. These are mainly applicable to low mercaptan content stocks and have drawbacks such as colour formation and loss of stability.

Some advances have been made in equipment. Rotating disk contactors are gaining ground for extraction systems in place of conventional pump mixer-settlers and packed columns. Electrical precipitation methods are being widely installed for acid and soda washing to reduce chemical treatment losses and produce haze-free products.

Chemical treatment continues to be an active field, but during the last five years substantial developments have occurred in hydrogen treatment, and this is beginning to challenge the position of some of the more conventional processes.

HYDROGEN TREATING PROCESSES

The expansion of catalytic reforming capacity has made large quantities of hydrogen-rich gas available for hydrofining operations, and a variety of processes have been developed to make full use of this relatively cheap hydrogen. The quantity available is substantial, varying from approximately 350 to 500 s.c.f/brl catalytic reformer feedstock. The purity ranges from approximately 70 to 85 per cent mol hydrogen, a typical composition being as follows:

Hydrogen	80·0% mol
Methane	13·5% ,,
Ethane	4·0% ,,
Propane	1·5% ,,
Butane	1·0% ,,

Desulphurization, olefin saturation, quality improvement, and the removal of trace contaminants

are the principal objectives of catalytic hydrogeneration. The main developments have been with processes to treat catalytic reformer feedstocks and upgrade middle distillates. Attention has also been given to the refining of lubricating oils, specialities, and catalytic cracker feedstocks. The advantages of hydrogen treatment over conventional processes are high yields, excellent product qualities, and the elimination of problems associated with the disposal of acid sludges and spent clays. Mixed oxides of cobalt and molybdenum on alumina are almost exclusively used as catalysts. Catalyst regeneration is carried out by burning off process carbon at relatively high temperatures using steam and air, or inert gas and air mixtures. This operation is straightforward and effects full recovery of catalyst activity. The main process variables are hydrogen partial pressure, temperature, space velocity, and gas rate. These variables are not simply related, and considerable experimentation is usually necessary to determine optimum conditions.

Hydrofining Naphthas and Kerosines

Treatment of catalytic reformer feedstocks constitutes the largest single use of catalytic reformer hydrogen. With high severity catalytic reforming, feedstock impurities such as sulphur, nitrogen, metals, organic chlorides, and unsaturated hydrocarbons have pronounced effects on catalyst life and activity. Modern catalytic reformers include a feed pretreatment section which reduces these impurities to very low levels by hydrogen treatment over conventional desulphurization catalysts. Middle East naphthas, apart from sulphur, are remarkably free from impurities. Very mild pretreatment conditions only are required to reduce the sulphur content, and hydrogen utilization is low, approximately 30 s.c.f/brl. Typical results obtained with Kuwait naphtha are shown in Table IX.

TABLE IX

Hydrofining of Catalytic Reformer Feedstock

(Kuwait naphtha 85°–175° C ASTM)

	Feed	Product
Specific gravity at 60° F/60° F	0·7425	0·742
Sulphur, % wt	0·042	0·0003
Nitrogen, p.p.m.	< 1	< 1
Arsenic, p.p.b. (1×10^{-9})	< 1	< 1
Lead, p.p.b. (1×10^{-9})	<20	<20
Copper, p.p.b. (1×10^{-9})	<20	<20
Organic chloride, p.p.b. (1×10^{-9})	< 1	< 1
Bromine number	0·3	0·2

Raw kerosine from some crudes is colour-unstable and cannot be refined to a good colour by conventional processes such as copper chloride or plumbite. A 1–2 per cent volume wash of 98 per cent sulphuric acid is conventionally used for such materials, but hydrofining now offers an alternative. Under mild hydrofining conditions kerosines equal in quality to acid-treated products can be produced for hydrogen consumptions of the order of 30 s.c.f/brl. Typical results obtained with a colour-unstable kerosine are given in Table X. Burning quality and colour stability show marked improvements.

TABLE X

Hydrofining Colour-Unstable Kerosine

	Feed	Product
Specific gravity at 60° F/60° F	0·8025	0·802
Sulphur, % wt	0·20	0·001
Doctor test	Positive	Negative
Odour	Sour	Good
Char, mg/kg	20	8
Colour Saybolt	14	+30
Colour after aging test	Dark	+30

Distillate material up to kerosine requires only mild hydrogen treatment for refining. The modern practice is to process a wide range fraction in a distillate hydrogen treater and distil the hydrofined product to give refined gasoline and catalytic reformer feedstock as tray cuts, and refined kerosine as a bottoms product. This method of treatment can be readily integrated into a single unit comprising crude distillation, distillate treatment, and catalytic reforming. Combination units of this nature show savings in refinery equipment over conventional plant layout.

Speciality products, such as special boiling point solvents and white spirit, are required to meet very stringent specifications regarding odour, corrosivity, and stability. These qualities are conventionally achieved by sulphuric acid treatment followed by redistillation, but suitable conditions for hydrogen treatment have now been established. Re-running is usually necessary to meet the exacting requirements of odour. Typical results are shown in Table XI for refining a Middle East white spirit by hydrogen treatment.

TABLE XI

Hydrofining of White Spirit

	Feed	Re-run product
Specific gravity at 60° F/60° F	0·790	0·786
Colour Saybolt	+14	+30
Total sulphur, % wt	0·12	0·001
Mercaptan sulphur, % wt	0·016	Nil
Copper corrosion at 100° C (3 hr)	No. 1	No change
Odour	Sour	Good

With light distillate feedstocks with end points of up to approximately 250° C, catalyst deactivation is very slight and regeneration is not normally a process

requirement, but facilities are normally included in equipment designs to safeguard against plant upsets.

Hydrofining of Diesel Fuels

Most Middle East gas oils are relatively high in sulphur content, and catalytic desulphurization for the production of low sulphur automotive diesel fuels is of growing importance. The first hydrofiner for this duty was commissioned in March 1955 in the British Petroleum Kwinana refinery, Western Australia. A large number of other gas oil hydrofiners have since been commissioned in Europe and the U.S.A., and a variety of successful process conditions have been developed. The range of these conditions is shown in Table XII.

TABLE XII

Commercial Diesel Oil Hydrofiner Conditions

	High	Low
Pressure, p.s.i.g.	1000	200
Temperature, ° F	800	600
Space velocity, V/V/hr	8·0	1·0
Gas rate, s.c.f/brl	4000	500
Catalyst: mixed oxides of cobalt and molybdenum		

Straight-run distillates in the gas oil boiling range from Middle East crudes have sulphur contents of up to approximately 1·3 per cent wt sulphur. Hydrodesulphurization results in a fall in specific gravity which is proportional to the amount of sulphur removed. The extent of this is shown in Table XIII for the desulphurization of Kuwait gas oil.

TABLE XIII

Desulphurization of Kuwait Gas Oils

T.B.P. range ° C	Sulphur content, % wt		Specific gravity 60° F/60° F	
	Feed	Product	Feed	Product
200–313	0·93	0·1	0·829	0·820
200–350	1·02	0·1	0·832	0·822
230–350	1·20	0·1	0·840	0·828
250–350	1·32	0·1	0·8455	0·8325

Small quantities of catalytic cracker cycle stock or thermally-cracked gas oil can be added to hydrofiner feedstocks to improve specific gravity. This is a common feature of gas oil hydrofiner operation, which also improves pour point. The hydrofined mixture of straight-run and cracked gas oils is of excellent quality. Hydrofining, apart from sulphur reduction, effects improvements in colour, odour, carbon residue, stability, and diesel index. Typical commercial results for high pressure hydrofining are shown in Table XIV.

TABLE XIV

Hydrofining of Middle East Gas Oils

	Straight-run		Straight-run light cycle oil	
	Feed	Product	Feed	Product
Specific gravity at 60° F/60° F	0·8375	0·8265	0·844	0·831
Colour, ASTM	1½	1	1½	1
Pour point, ° F	5	5	0	0
Carbon residue (on 10 per cent residue), % wt	0·05	0·01	0·08	0·02
Diesel index	59	66	55	61
Sulphur, % wt	1·0	0·1	1·30	0·1
Hydrogen consumed, s.c.f/b	—	100	—	225

The designs developed range from liquid to vapour phase operation and include the use of once-through and recycle hydrogen flow. The simplest plant results from once-through operation at a pressure just below that at which hydrogen is available from a catalytic reformer. This avoids the use of a make-up and recycle gas compressor. This method of operation requires low operating pressures and low operating temperatures to avoid frequent catalyst regeneration. For moderate desulphurization the once-through process is attractive. Relatively high gas flows are necessary to maintain reasonable on-stream periods between regenerations. For severe desulphurization and where insufficient hydrogen is available for a once-through flow, recycle of hydrogen gas is necessary.

Desulphurization is brought about by the removal of sulphur as hydrogen sulphide. The presence of this gas at high temperatures introduces a number of corrosion problems. These have been overcome by the use of alloy steels. Corrosion by hydrogen sulphide not only results in excessive wear, but the corrosion products are carried forward and block the catalyst. Guard chambers have been installed to prevent this.

Miscellaneous Hydrogen Treatments

The principal steps in the production of lubricating oils are deasphalting to remove resinous and asphaltic materials, solvent extraction to remove aromatic type hydrocarbons, dewaxing to remove wax, and a finishing treatment. The conventional finishing treatment comprises contact with clay at high temperatures for colour and stability improvement. Recent developments have shown that a mild catalytic hydrogen treatment is a satisfactory substitute for clay finishing. The equipment required is simple, yields are substantially 100 per cent, and problems associated with clay disposal are avoided. Hydrogen treatment is not as selective as clay contacting, but satisfactory colour and oxidation stabilities can be achieved for a wide range of lubricating oils. Desulphurizing conditions are avoided to prevent molecular breakdown and loss of viscosity, and

hydrogen consumptions are accordingly low. Several commercial plants are in operation.

Catalytically-cracked gasolines from high sulphur crudes have relatively high sulphur contents and consideration has been given to the desulphurization of catalytic cracker feedstocks to improve the lead response of cracked gasolines. Gains of up to 2·0 O.N. can be achieved, and yield improvements are claimed. Hydrogen consumptions are high. Desulphurization of catalytically-cracked gasolines with hydrogen is not readily possible because saturation of olefins occurs with a resultant drop in O.N. Selective catalysts which avoid hydrogenation, but which remove sulphur in the presence of hydrogen, are being developed.

Power kerosine or tractor vaporizing oil normally contains a proportion of highly aromatic material. Sulphur dioxide extract from the production of high smoke point kerosine is a suitable component for this purpose, but extracts from Middle East kerosines have sulphur contents of the order 1·0–1·5 per cent wt. The sulphur can be conventionally reduced by acid treatment. The Autofining process is an alternative possibility for this duty. This is a catalytic desulphurization process which supplies hydrogen from naphthenes present in the feedstock and does not therefore require extraneous hydrogen. With neat kerosine extract, on-stream periods of up to 250 hours are obtained before regeneration is necessary. With power kerosine blends, on-stream periods of up to 2000 hours are obtained. Regeneration is simple and similar to that adopted in diesel oil desulphurization processes. The cobalt molybdenum catalyst is extremely rugged. The original charge of catalyst in the autofiner at the BP

TABLE XV

Treatment of Power Kerosines by Autofining

	Raw extract	Autofined extract	Raw blend	Autofined blend
Specific gravity, 60° F/60° F	0·870	0·862	0·824	0·819
ASTM, °C	160–290	155–290	155–265	155–265
Total sulphur, % wt	1·30	0·45	0·65	0·10
Mercaptan sulphur, % wt	0·04	Dr Neg.	0·03	Dr Neg.
Aromatic content, % wt	78	78	38	39
Colour, Saybolt	7	18	10	21

Llandarcy refinery has been in use for five years without any change in activity. Typical results for this operation are given in Table XV.

MISCELLANEOUS DEVELOPMENTS

It has not been possible in a broad review to include all the innumerable developments that have taken place during the last five years. A number of significant developments have had to be omitted. In particular, in the lubricating oil field, passing reference should be made to the application of the urea adduction process, the use of higher ketones for dewaxing, and the application of centrifugal extractors and rotating disk contactors for solvent treating. In the distillation field, progress continues in the design of vapour–liquid contacting devices. Higher fractionating efficiencies, smaller tray spacings, and smaller columns are being made possible by the use of perforated or sieve-type trays. These are very suitable for fractionating light hydrocarbons and are finding increasing application in equipment for the production of *iso*paraffins as motor and aviation gasoline components. On the research side, radioactive tracer techniques are beginning to make a substantial contribution to process studies, especially in the field of fluidization. Considerable developments have taken place in electronic equipment and instrumentation. The fully automatic refinery which tests and blends its products is foreshadowed. Statistical mathematics and linear programming techniques are finding a wide application in refinery operations. The application of computers to refinery programming and plant design is receiving increasing study. These new techniques add speed and precision to the solution of very complex problems and substantial developments in the efficient design of refinery equipment and in the technical efficiency of refinery operations are anticipated. It is perhaps too early yet to assess the full significance of the new trends, but it seems likely that they will become of increasing importance and will play a major part in maintaining, if not increasing, the remarkably high rate of development achieved throughout the oil industry during the last five years.

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DISCUSSION

Dr J. A. Berriman: I was not very clear whether the author's comparison of yields from Kuwait crude in the U.S.A. and Western Europe was on a weight or a volume basis. It is a small matter and the statistics are probably not very exact anyway.

In Table IV I noticed that Mr Newby thermally reforms a naphtha feedstock (i.b.p. presumably 100° C or greater) and obtains a product having what I thought was an unusually high volatility of 32 per cent at 100° C; possibly it was butanized.

However, I would certainly agree that wonderful things can be done nowadays with the Platforming reaction and, indeed, the 8 catalyst has provided refiners with a most invaluable tool in and around the 100-octane field.

I like the account of catalytic cracking. I think that as regards feedstock preparation, rather than improving the propane extraction route, there is a more marked tendency towards improvements in flash distillation methods, *e.g.* by the use of mist extractors of either the mat type, grid trays, or cyclone type separators.

As regards the chemical treatment section, I cannot help thinking that if one asks a man how he sweetens his gasoline, then one knows pretty well by the answer what company he works for. At any rate, it is almost inevitable that one can have a variety of preferences for one's gasoline treatment. Even, in some cases, a preference for the so-called obsolete doctor test.

I was a little unsure what the author meant by catalysed cresylate solutions. The only thing which sprang to my mind was the Tannin process, but I was not really sure about that. Further, there was some kind of inference that in the air solutizer process colour formation and loss of stability often ensue, but nevertheless it is possible to get good results using such a process with cat cracked gasoline. I think the author is referring to operation on straight-run feedstocks?

In regard to the remarks on hydrogen purity, I think on Western feedstocks one can obtain rather better than 85 per cent mol purity; over 90 per cent has been obtained in certain cases.

There is one small point on which someone may care to comment. Mr Newby made a passing reference to the octane number of benzene, the inference being that the blending leaded octane number was over 100. I know there have been many variable results with benzene, some ranking down as low as 80 for leaded blended numbers. I would like to hear any comments on that.

W. J. Newby: The answer to Dr Berriman's first question is that the yields are presented as volumes, not weights.

Referring to the second question, a volatility of 32 is a reasonable figure.

On the question of chemical treatments, the actual processes I mentioned have been referred to in the literature. There are a number of patents covering the use of various organic chemicals and metals to catalyse the oxidation of mercaptans in the presence of cresylate solutions. In the BP Kent refinery we use a cresyllic soda solution, which is catalysed by a small amount of copper. In these circumstances, we get quite rapid conversion of mercaptans. But the process is used for straight-run materials and with them one does get a small colour degradation. In the laboratory work I have seen and in commercial practice this does seem to be a general feature of any catalysed sweetening process of this type.

Referring to the fourth point, hydrogen purity, Dr Berriman is perfectly right. A hydrogen concentration on a mol basis very much higher than the figures I have shown can be obtained and, of course, the lower the severity of catylytic reforming, in general the higher is the hydrogen concentration in the excess gas.

In regard to the final point, I was referring to the research leaded octane number as a "blending octane number." In other words, the contribution that benzene makes to the motor gasoline blend, rather than the octane number if one tests the benzene on its own.

S. J. W. Pleeth: I notice, in the hydrofining of gas oils, that while the hydrofining has the effect of increasing the diesel index, it also has the effect of reducing the specific gravity.

Which is the most important thing from the point of view of the purchaser of gas oil? Does he want more B.t.u.'s per penny of product, or does he prefer a better diesel index?

W. J. Newby: I think the answer to that is that, like all these things, there is no simple answer. Probably something of the order of 30 per cent of the gas oil is present as molecules which contain sulphur. It is not just sulphur as elemental sulphur, but as organic compounds, or organic hydrocarbons containing sulphur. Therefore, if that sulphur is removed, we either reduce the gravity because we have to close rings and substitute hydrocarbon instead of sulphur or, alternatively, break the molecule and get a breakdown product. For these reasons one is always going to be faced with a drop in gravity.

The increase in diesel index is not regarded as significant. That is merely a bonus of the process. The most important thing is to reduce the sulphur. It is important that the gravity should be maintained, particularly while customers buy their gas oils on a volume and not on a weight basis. From a customer point of view, a high specific gravity is obviously preferred, and this can be achieved by using either thermally cracked gas oils or catalytic cracker cycle stocks. These materials are higher in specific gravity, because they contain more aromatic type materials. If these are blended with straight-run gas oil, one finishes up with a desulphurized gas oil of improved specific gravity, but one will also, because they are aromatic materials, have reduced the cetane number. So, by and large, one is back where one started on cetane number, but, with luck, has gained a little on specific gravity.

Dr G. B. Maxwell: My question arises from Mr Newby's last remark about the incorporation of thermally cracked gas oil in blends with straight-run gas oil for hydrofining for sulphur reduction. I think there is still a case to be made for vis breaking and wax cracking of residues, from Middle East crudes in particular, in order to increase the overall quantity of middle distillates in line with the point that Mr Newby made earlier in his paper. If one does so, of course, one is not only making a certain amount of thermally cracked gas oil, but unfortunately one must also make some thermally cracked spirit, and that is not only rather dirty material to handle, as we all know, but also has rather a low octane number.

I would like to ask the author if any work has been done on incorporating thermally cracked spirit with straight-run naphtha as a feed to a cat reformer, in the cases where one has a feed pre-treatment unit to get the

sulphur and other deleterious material out of it. In such a case, would he expect to get a somewhat similar octane number product from a blend containing not too much thermally cracked spirit?

W. J. Newby: Dr Maxwell is quite right that vis breaking and thermal cracking is a way of augmenting middle distillates. He is also right that it has one disadvantage as far as the future is concerned, that the thermally cracked gasolines are of low octane number. There is also another feature, they are also very difficult to sweeten. Referring specifically to his question, a fair amount of work has been done which shows that thermally cracked gasoline or vis breaker gasoline can be included with cat reformer feedstocks. The olefins are saturated, rings are closed, and a number of these rings are in a suitable form for conversion to aromatics. I believe that in a number of situations in the U.S.A. it is quite common practice to include a percentage of that type of material, either coker gasolines, vis breaker gasolines, and so on, along with the reforming feedstock. The only disadvantage it has, of course, is that it does use a fair amount of surplus hydrogen, which may be required for desulphurization. However, it is now regarded as quite a conventional route, and without any special precautions, I think I am right in saying that something up to 10 to 15 per cent of coker gasolines or similar materials may be included and will result in a substantial octane improvement by processing along with the catalytic reformer feedstock.

Dr J. W. T. Jones: We have seen the introduction of hydrofining to improve gas oils and, working down the scale of value in products, I would be interested to know if Mr Newby considers there are any significant movements towards treatment of residual products to fit them for the severe duties of special uses, *e.g.* as turbine fuels.

W. J. Newby: Dr Jones has actually raised quite a large subject. I suppose that the difficulties with furnace oils are, first, sulphur and, secondly, metals. Both can be removed from residual fuel oils. The main metal contaminant is generally vanadium, and for some special requirements, *e.g.* in the glass industry, both low sulphur and low metal content fuel oils are required. When I said they can be removed, this can only be done at a price. The process equipment is expensive and the hydrogen requirement is extremely high. There are a lot of pros and cons about the sulphur content of fuel oils. The easiest way to do it, of course, is to use a crude oil which has a low sulphur content. That is the easy way. Apart from special requirements, such as steel production, low sulphur fuels are requested normally for reasons of corrosion, and to enable the maximum recovery of heat from economizers which corrode if temperatures are too low.

BP have recently developed an ammonia injection process which safeguards economizers under these conditions. To my mind, this goes some way towards offsetting the necessity of having to reduce the sulphur content from residual fuel oils. If the oil industry were faced with having to produce large quantities of fuel oils with very low sulphur contents, it could not be done economically and I am quite convinced that industry in general would prefer to accept the higher sulphur contents.

V. Biske: I was interested in the author's mention of the use of hydrogen as a substitute for clay in finishing treatment of lubricating oils. Could he tell us whether such treatment does remove small traces of impurities, of particular importance in certain specialized products? I have in mind trace impurities which affect electrical properties, such as power factor and resistivity, of insulating oils, and impurities affecting demulsification, of importance for turbine oils. Are such slight contaminants removed by hydrogen treating as efficaciously as by conventional clay treatment?

W. J. Newby: The main incentive for the work on hydrogen treatment of lubricating oils is not so much to improve qualities over and above what they are today, but to find a cheaper process. Economics show that hydrogen treatment is cheaper than the ordinary conventional clay treatment. It also does away with the necessity of having to dispose of large tonnages of spent clay. I have seen figures from which one can conclude that the trace materials have been satisfactorily removed. For example, steam demulsification numbers are comparable with clay-treated products. Colour stability in many cases is better than for clay-treated materials. The B.A.M. oxidation tests are also equally satisfactory. However, taking all the results collectively that I have seen, I am left with the impression that hydrogen treatment is not as selective as clay. It can do as good a job, but taking it all round, clay does a more precise job for those trace materials which I think you are worried about.

Dr E. B. Evans: Would Mr Newby consider that within the last five or ten years there has been what might be described as a major advance in refining? I mean major in a sense comparable to that of, shall we say, the introduction of fluidization, fluid cat cracking, or catalytic reforming. I know that the regenerative processes which have been introduced constitute a great advantage over the original catalytic reforming, as introduced with platforming more than ten years ago now. However, if one looks at the patent literature a large proportion of the inventions seem to cover comparatively small improvements, although many of them are obviously of real value. Surely, what has been done in the last five or ten years adds up mainly to the constant striving for detailed improvement, with the idea of reducing costs and improving economy of known processes. The re-arrangement of a plant to get better heat economy, altering the length of transfer line, a modification of stirring arrangements, and so forth are perhaps not in themselves major developments, although they may result in cheapening a process or improving its efficiency or economy.

Is it fair to describe the achievements of the last five or ten years as mainly that, or would you consider that there has been a considerable number of really major developments in that period?

W. J. Newby: I think that, looking back over the last five years, there are two distinct types of improvements. In the first category, there are improvements which have helped to cheapen plants and make them more efficient. In alkylation, catalytic cracking, and also in distillation, such improvements have been substantial. They may not appear so when one reads about them in the patent literature or in the journals, but if one builds refineries, say every four to five years, one is impressed with the extraordinary jump forward that has occurred in such equipment. I do not regard these as major advances, because I think they are logical developments, which will always occur within the industry.

In the second category, as to what has been a major advance in the last five years, I would say the develop-

ment of catalytic reforming. This a major process which has made just as big an impact on the industry as thermal reforming must have done in the early 1900s, and also as more recently did catalytic cracking. Even if UOP did announce their process in 1949, it was not really until 1952 that it was first commercially installed, which is why I consider that catalytic reforming, as we now know it, really belongs to the last five years. The first plant was designed for an octane number of the order of 85. To-night we are talking quite happily of octane numbers of around 95, and even up to 100. This has not been achieved by using the same plant, the same equipment, or the same catalysts that were developed originally. There have been very substantial advances in catalyst formulation, know-how in plant operation, and how to handle the small amount of trace elements which previously stopped very high octane numbers being obtained.

A second major development in the last five years has been the introduction of hydrogen treatment. I am quite sure that in the next five years we shall see the spreading of the use of hydrogen to very many more processes than at present. It is a most efficient work-horse. It does a very good job on sulphur. It does extremely well on a number of trace materials. I am convinced we should regard both these processes, catalytic reforming and hydrogen treatment, as two very big steps forward. Nevertheless, at the same time I think we should also bear in mind the substantial contribution that has been made, and always will be made, to existing processes by marginal year-to-year improvements, because they do, in the three cases I have quoted, catalytic cracking, alkylation, and distillation, add up to considerable progress.

Dr G. B. Maxwell: Do you regard C_5 and C_6 size isomerization as being a major event?

W. J. Newby: When Dr Evans asked his question, quite a lot of processes ran through my mind, but I am afraid that one did not. Isomerization is a process which has been known now for very many years. During the war, of course, the process was used for augmenting *iso*butane production for alkylation. The isomerization reactions over various catalysts have been explored in laboratories for many years, and some of the existing processes tucked away for a number of years. At the present time it is opportune to consider these processes afresh, particularly for the circumstance existing in the U.S.A. I believe we shall not have to consider these processes in our own hemisphere for many years. In the U.S.A., where something of the order of 40 to 45 per cent motor gasoline is required and where pool octane numbers are considerably higher than in the U.K., refiners are faced with an embarrassing quantity of low volatile material, which cannot be fitted into the gasoline picture unless it is upgraded. Therefore, I think refiners are being forced into isomerization. There is another reason and that is the question of road octane number. How one defines a road octane number, or even how one measures it, is open to a certain amount of debate. But from the American picture it is being demonstrated that better road performances, or better road octane numbers, are obtained with materials which have low research appreciations. This is a special feature of *iso*paraffins; they have very low research appreciations, which help to offset the high research appreciations of aromatics obtained from catalytic reforming.

D. H. Peel: Dr Berriman has mentioned benzene. Whatever the effective octane number may be in any particular blend, benzene is a valuable high octane number component of motor gasoline, because it is low boiling and provides this octane advantage in the front end of the gasoline. It would therefore seem to be a good idea to try to make more benzene. I wonder if Mr Newby could comment on the possibilities of producing benzene by de-alkylation of higher boiling aromatics.

W. J. Newby: I think the answer is that it is generally known how to de-alkylate aromatics, but it is expensive. I am not aware of any commercial operation for the de-alkylation of high aromatics, but I am quite sure that most companies have had a look at it and in fact, if there is not a commercial process, I think everybody must have come to the same conclusion—that it is a very expensive operation.

I would not like this meeting to go on record without us knowing what the octane number of benzene is and I am quite sure that Mr Greaves would be able to tell us.

CONTRIBUTED DISCUSSION

W. C. Greaves: The answer depends on who does the testing and how it is tested. The research octane rating of neat benzene was discussed in several papers [1–4] presented at the "Symposium on Evaluation of Anti-knock Quality of High Octane Fuels," sponsored by the Coordinating Research Council, 5–6 December 1956. The octane ratings quoted varied between 107 and 120+. The reasons for these differences are discussed in the papers referred to.

Data on benzene in various blends were also presented at the above-mentioned symposium, and have also been presented by the API [5] and elsewhere.[6] The lowest derived blending research octane number would appear to be a figure of 90 for a blend of 40 per cent benzene in 60 O.N. primary reference fuel,[4] while the highest appears to be a figure of 118 for a blend of 50 per cent benzene 50 per cent *iso*-octane.[1] Boyd, Stack, and Stahl quote blending research octane numbers in typical motor gasoline blends of 105–106 neat and 111 with 1·2 ml TEL/IG.

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ADHESION IN BITUMINOUS ROAD MATERIALS: A SURVEY OF PRESENT KNOWLEDGE *

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SUMMARY

The extent of present knowledge on adhesion in bituminous materials is surveyed. Much of the material for the survey has been provided by the literature listed in Road Research Laboratory Library Bibliography No. 81, although some additional material is also reviewed. The subjects covered include adhesivity in the absence of water, factors affecting adhesion in bituminous road materials, the physico-chemical properties of the system water–stone–binder, adhesion tests, and the effect of additives on adhesion. The final section of the survey reviews those aspects of the subject on which further information is required to complete the general picture of adhesion in bituminous materials.

INTRODUCTION

THE properties of bituminous materials are much affected by the way in which the adhesive or binder is used, by the type of binder and the nature of stone employed, and by the way in which factors such as external stress or atmospheric conditions may influence the adhesive bond. Neither bitumen nor tar can be regarded as an ideal adhesive, but, in general, when proper precautions are exercised, both are adequate. There are occasions, however, when the adhesive bond may fail and the durability of the bituminous material may be seriously affected; a considerable amount of effort has therefore been put into the study of the subject. Up to the end of 1955, over 400 papers and reports on adhesion in bituminous materials had been published. A recent bibliography [1] lists most of these papers. This review is based on the material in that bibliography together with some additional material, including recently published papers and hitherto unpublished work; it is intended to summarize the present state of knowledge on adhesion.

FACTORS AFFECTING ADHESION IN BITUMINOUS ROAD MATERIALS

It is not surprising that a number of factors may influence the behaviour of a material as complex as that of a mixture of a bituminous binder and stone. The requirements of a bituminous binder as an adhesive were discussed by Lee,[2] who pointed out that a road binder meets conditions which are rather different from those met by most adhesives; for example, the surface of a roadstone is rarely either clean or completely dry.

Wetting of Roadstone by Bituminous Binders

The wetting of a dry stone by a binder is controlled largely by the physical properties of the binder and particularly by its viscosity. At one time there was some discussion as to whether viscosity or surface tension was the more important property.[3, 4]

The surface tensions of normal road-tars and bitumens are in the region of 30 dynes/cm,[5, 6] and all can be used to wet roadstone without difficulty provided an appropriate viscosity is chosen. It can therefore be deduced that surface tension is not a major factor in the wetting of dry stone.

The viscosity of the binder, however, is of great importance. Both bitumen and tar are highly viscous fluids and their consistency is markedly affected by temperature. Even the most viscous binder will spread on a perfectly clean surface, and so wet it, if given enough time; for practical purposes, however, it is necessary for the viscosity of the binder to be so adjusted that wetting occurs almost instantaneously. When the aggregate is dusty the control of the viscosity becomes even more critical, because there is always a tendency for the layer of dust to be coated preferentially by the binder. In the case of a surface dressing, the use of very dusty chippings may well result in non-adhesion of much of the stone because of the inability of the binder to penetrate through the layer of dust.

When the stone is damp or wet it is normally almost impossible to achieve adequate wetting by a bituminous binder, although application of high pressures has been shown to help bitumen to displace water from the stone.[7] The artificial drying of the stone is therefore normally an essential preliminary to the making of bituminous mixtures; with surface dressings adhesion is usually dependent on the natural drying-out of the spread chippings if they were initially wet. Special processes which have been developed to overcome these difficulties are discussed later in the paper.

Strength of the Adhesive Bond under Dry Conditions

It has been assumed by most workers that the only important problems in adhesion arise when water is present. Thus there are but few studies of the dry-

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adhesivity or binding strength of bitumen and tar. Kirschbraun [8] described an apparatus for measuring the strength of the bond between a wooden ball covered with silk and a tar. Subsequently, suggestions were made for the improvement of this technique by replacing the ball by a cube of stone.[9] Hermann [10] pointed out that the presence of dust on the surface of most roadstones makes measurement of dry-adhesivity of little practical significance. However, within a limited field of application, comparative tests of adhesivity may be of some value; such tests have been used to examine the rate of hardening of binders in those cases where it can be assumed that the resistance to separation of a solid from a film of binder is a function of the viscosity of the binder.[11,12]

Under practical conditions on the road it is unusual for the bond between a binder and a stone to fail at their interface for reasons other than the displacement by water of the binder from the surface of the stone. Nevertheless, cases are known where old and weathered binders may fail in adhesion; [13] it is much more usual when severe weathering has taken place for there to be a cohesive failure within the film of binder.

Strength of the Adhesive Bond under Wet Conditions

While breakdown of adhesion under dry conditions is extremely rare, there is a serious risk of displacement of the binder from the stone surface if water is permitted to reach the interface. The rate at which displacement will occur in these circumstances will depend, among other factors, on the viscosity of the binder. Although at the temperature of application the binder must be of a sufficiently low viscosity to ensure adequate wetting, it must also, on cooling to road temperature, reach a sufficiently high viscosity to retard displacement of the binder from the stone surface if water penetrates into the material. In practice, this increase in viscosity is rarely achieved in a sufficiently short space of time, and therefore most bituminous materials are susceptible to damage for at least a short period unless they have been designed to exclude or resist water. The introduction of filler alone has markedly reduced the tendency of the material to strip. However, in general, it is desirable to take some more positive step to protect the material against water by one of the methods outlined later in this survey.

The chemical type of the binder used in a coated material seems to have some influence on the performance of the material, although this is not invariably so. Thus, for example, it is rare for stripping to be observed in coated macadam surfacings manufactured with a tar binder, although most types of bitumen (but not all) will show some stripping under comparable conditions. Lee [2] showed by means of measurements of contact-angles that a road tar containing a relatively high amount of phenols (vertical-retort tar) was better able to withstand displacement from a stone surface by water than was a tar of low phenol content (horizontal-retort tar), and this tar was in turn more resistant to water than a straight-run bitumen. However, the differences in resistance to water between binders of various chemical types are not usually sufficient to produce differences in behaviour under the more extreme conditions of use. For example, most types of binder appear to be susceptible to stripping when used in coated macadam base courses into which water may penetrate, and there is no evidence to show that there is any significant difference in the adhesive behaviour of either tar or bitumen under wet conditions in a surface dressing.

The type of stone employed in a bituminous mixture may influence the adhesive behaviour of the material, but much of the work showing that different stones and different types of stones have markedly different adhesive properties is based purely on laboratory tests. Practical experience, resulting from observations made on roads by the Road Research Laboratory, shows that the effect of the general nature or type of the aggregate on stripping has been overrated by many authors. Some calcareous and siliceous aggregates undoubtedly exhibit stripping on the road less frequently than do the majority of aggregates, but relatively few aggregates are known which are completely resistant to the action of water under all conditions of practical use. For this reason it is not possible to generalize about the behaviour of classes of aggregates. In particular, the well-known and often quoted rule that " acidic " rocks (high silica content) are vulnerable to stripping whereas " basic " rocks (low silica content) are not, is quite wrong.

Several attempts have been made to measure the pH of water when in contact with roadstones, and it is clear from most of the results that where differences in pH are observable they are small and of little significance.[14,15] Moreover, in general, however " acidic " the aggregate, the pH of water in contact with the stone is never much lower than 7.

In spite of the immense amount of literature concerning laboratory tests of adhesivity and methods of improving adhesion in bituminous materials, comparatively few accounts have been published concerning the types of damage to bituminous roads which are caused by water. Brief accounts are available of failures in surface dressings,[16] bitumen and tar macadam surfacings,[13,17] and asphaltic concrete.[18]

Since almost all the problems on adhesion in bituminous materials that are of practical importance are caused by the presence of water, the permeability towards water of the bituminous mixture as a whole must be considered. Where a material is totally

impermeable to water, stripping does not occur. This is the case with a properly manufactured and well-compacted hot-rolled asphalt.[17] Where a material is open to attack by water, stripping is always a potential danger, and if it occurs there is always a chance that the material will fail owing to the failure of the adhesive. However, in some materials in which stripping is common for this reason, such as, for example, bitumen macadam, failure is nevertheless relatively infrequent because of the inherent mechanical stability of the stone structure, which is adequate to resist most of the disruptive stresses imposed upon it by traffic.

The effect of traffic on the behaviour of a bituminous material may be to encourage stripping, but not necessarily failure, as in the case of coated macadam, or to promote failure, as in the case of both surface dressings and coated-macadam surfacings. The risk of failure of a surface dressing caused by wet weather is small on roads carrying a relatively small amount of traffic; the binder may be displaced from the stone by water, but unless the layer of stone is disturbed by traffic it will re-adhere when the road is dry. Traffic tends to throw the chippings off the surface and so destroy the dressing. Again, in coated-macadam surfacings, stripping is usually observed in the areas of the road traversed by traffic. Where the material is not subject to the regular action of traffic on the road, *e.g.* close to the channel or between bollards, it is unusual to find stripping even when a sample of the identical material taken from the traffic lanes may be severely stripped. Instances have also been reported of damage to roads caused by stripping in base-course macadam where the stripped material has moved under traffic and so caused deformation of the surfacing. The problem of stripping in base-course materials has so far received very little attention, although it is known that many practical instances of stripping exist.

The mechanism of stripping in road materials is not well understood. The classical theory of displacement of one liquid by another on a solid surface (see later) has sometimes been quoted to explain the displacement of binders from stone surfaces, but such an explanation does not deal satisfactorily with several of the effects observed in coated materials. The theory is reasonably adequate for explaining the behaviour of surface dressings in wet weather, although even here there is not complete agreement among all workers.[19] As mentioned above, traffic may play an important part in the stripping process in coated materials and, further, it has been suggested that elastic deflections in the road structure under traffic may be of importance in the process of failure of stripped surfacings.[17] Another feature of the classical theory of wetting, which is unsatisfactory when applied to coated materials, is that it fails to explain how stripping is initiated when the stone is completely coated with binder.

The suggestion has been advanced that finely divided mineral matter may play a part in stripping by promoting emulsification of binders in water.[20,21] Ebberts [20] has claimed that siliceous fillers are undesirable for this reason, and he preferred to employ calcareous fillers, which show less tendency to act as emulsifiers. Wilhelmi and Schultze,[22] on the other hand, have demonstrated by a series of experiments in the laboratory that it is possible for water to penetrate a film of binder and thus initiate stripping at the stone/binder interface. Presumably a system of stone, water, and binder might be inherently unstable, and the effect of traffic could well be to cause the fracture of the film of binder and so enable stripping to be apparent. This theory would explain why stripping is frequently first observed at sharp corners and edges where the film of binder is thinner than elsewhere; in these circumstances it is likely that water may penetrate the film of binder more rapidly and the film of binder (already in a state of strain) would then be exceptionally unstable.

PHYSICO-CHEMICAL ASPECTS OF THE SYSTEM WATER–STONE–BITUMINOUS BINDER

The physical and chemical aspects of the interfacial system water–stone—bituminous binder have been studied by a number of independent workers, but so far the results obtained from these studies have not advanced our understanding of the system as much as one might have hoped. The major difficulty encountered in all the investigations has been that the bituminous binder has a high viscosity. Thus there has usually been the choice of working with a binder of unrealistically low viscosity in what amounts to a model system or using a system which, owing to the high viscosity of the binder, may not readily reach equilibrium within the time of the experiment. Although several reviews have appeared which seek to put the physico-chemical aspects of adhesion in their proper perspective,[2,13,23,24] it is useful at this stage to summarize our present knowledge and see where the various approaches to the subject have led.

The surface tensions of both bitumen and tar have been studied by several different techniques. Nellensteyn's work [6] with both bitumen and tar was based on the Jaeger maximum-bubble-pressure method, whereas Saal [5] used the du Noüy ring method for bitumen; the theory of the capillary rise of liquids has been applied in the methods of Léauté [25] and Mack.[26] Both Nellensteyn and Saal made measurements over a range of temperatures, but neither of the methods used was suitable for obtaining satisfactory results at temperatures below 100° C, because of the

effects of high viscosity. Their results agree reasonably well above 100° C, and are of the order of 25 to 30 dynes/cm, depending upon the temperature and the source of the binder. At 100° C there is a divergence in the results which Saal attributed to the high viscosity reached by the binders in Nellensteyn's experiments. Léauté's result with the capillary-rise method gave figures of nearly twice the magnitude of those obtained by most other workers. Perhaps the most useful set of measurements is that obtained by Mack,[26] who used a very elegant and simple technique. He measured the dimensions of free-hanging threads of bitumen at 20° C and obtained, by application of the theory of capillary rise, values for different types of bitumen ranging from 26 to 39 dynes/cm. He obtained similar results using the capillary-rise method itself, by measuring the surface tension of solutions of varying concentrations of bitumen in benzene and then extrapolating to pure bitumen. It is interesting to note that Mack's results at 20° C showed a greater variation in the surface tension of bitumens of different origins than is shown by the results of Nellensteyn and Saal at high temperatures. The results obtained by Mack are borne out by those of Traxler,[27] who measured, by means of the du Noüy method, the surface tension of crude petroleum oils over the range of temperatures between 26° and 85° C and obtained results ranging from 35 to 25 dynes/cm.

Mack also deduced the interfacial tension of bitumen against water from a series of measurements with solutions of bitumen in benzene. His results at 20° C ranged from 15 to 20 dynes/cm. Lee,[2] from calculations based on the dimensions of drops of bitumen and tar immersed in water, obtained results varying between 17 and 24 dynes/cm, which are in reasonable agreement with Mack. Saal [5] has also found a value of the order of 25 dynes/cm for bitumen/water, whereas Nellensteyn and Roodenburg [6] found values of the order of 30 to 40 dynes/cm for various binders against water.

The usual approach to the problem of adhesion has been along the lines of the classical theory of wetting, by trying to measure or deduce the contact-angle between the binder and the stone. The basic equation used in this approach has been that of Young and Dupré:

$$\gamma_{SW} - \gamma_{SB} = \gamma_{WB} \cos \theta$$

where γ_{SW}, γ_{SB}, and γ_{WB} represent the interfacial tensions between the stone–water, stone–binder, and water–binder phases respectively and θ is the three-phase contact-angle. As Harkins [28] has shown, this general approach to the problem of wetting is open to criticism and theoretical reservations, and, since one of the liquid components of the system, water, has an appreciable vapour pressure at the temperatures at which experiments are normally carried out, the above equation is almost certainly invalid. However, the term $\gamma_{WB} \cos \theta$, which represents the tendency of the two liquid components to spread against each other on the stone surface, is on its own not open to theoretical objection, and therefore the work based solely on this term as a measure of the tendency of water to displace a binder is theoretically sound. It is the practical difficulties of the determination of the spreading tendency which have led to the lack of certainty in the results. As mentioned above, the viscosity of normal binders leads to severe experimental difficulties and, further, it is almost impossible to obtain stone surfaces which are truly plane and yet are unchanged in their natural surface characteristics.

The measurement of contact angles is notoriously fraught with difficulties and uncertainties, and measurements with bituminous binders and water on stone surfaces provide no exception to the general rule. There have been two general approaches to the problem: one based on direct measurement of the contact angle, such as that used by Loman and Zwikker,[29] and Lee,[2] and the other based on a direct measurement of $\gamma_{WB} \cos \theta$, as in the method used by Hallberg.[30] Lee found that the contact angles of different binders on the same surface showed appreciable differences which were a function of the acidic content and general wetting properties of the binders. Thus the contact angle between a vertical-retort tar and a stone or glass surface in the presence of water was very much larger than that obtained with a residual bitumen under similar conditions. However, when he made measurements on different types of stone with the same binder he found that the magnitude of the contact angle depended on how the surface had been prepared (to give a plane finish) rather than on its origin. Hallberg's approach, although a valuable one and similar in principle to that of the Bartell displacement cell,[31] is limited in its application to rather fluid binders or oils, and to beds of finely powdered stone. The theoretical basis of the method is open to the same objections as those applying to the Bartell method.[28] However, Hallberg [32] has used his method to study the effect of the addition of surface-active agents to bituminous binders and has thus developed his concept of active and passive adhesion, the distinction depending upon whether the binder is able to displace water from a stone surface or merely itself resist displacement.

Andrews and his co-workers [33] have studied the spreading of bitumen and tar over the surface of water and aqueous solutions of inorganic salts by means of a surface-pressure balance. They found that the presence of oxidizing agents in the aqueous phase markedly increased the tendency of bitumen to spread over water. A bitumen reclaimed from a 20-year-old surfacing spread much more readily over water than did an unweathered bitumen. The weathered bitumen

spread over plain water with a speed comparable to that of unweathered bitumen over an aqueous solution of potassium permanganate. The spreading properties of binders over water have been discussed in great detail by Wilhelmi and Schultze,[22] who found that all bituminous binders are potentially able to form a spreading film on water. They consider that the properties which influence the speed of spreading are viscosity, surface tension, and interfacial tension. They believe that binders showing the greatest tendency to spread over water have the greatest power of adhering to stone. In spite of this, some binders which have good spreading properties are known not to have good adhesive properties; Wilhelmi and Schultze have shown by microscopic examination of the spreading films of such binders that small holes appear in the film which progressively enlarge to form a network; later the network breaks up to form droplets. They have also shown that if a dry glass surface is coated with a film of binder and then immersed in water, bubbles of water appear beneath the film of binder. It is possible after a few hours to strip the layer of binder from the glass even if a relatively hard bitumen has been used, and there is no trace of residual adhesion to the glass. When an adhesion agent is added to the binder, the formation of bubbles still occurs beneath the binder, but the treated film is less easy to strip from the glass.

Attention has been drawn on several occasions to the part which adsorption may play in the adhesion of binders to stone.[34-37] The same practical difficulty of high viscosity is encountered when studying adsorption as in other investigations. It has therefore been necessary to resort to the study of adsorption of bitumens from solutions in organic solvents. This approach has shown that different aggregates adsorb binders to different degrees and that there are some variations in the behaviour of different types of binder. However, the results of this work lose some of their value because the surface-areas of the stone powders used were not determined. In any case, although such studies may provide a useful qualitative guide to the adsorptive properties of stones and binders, the quantitative data obtained are rather restricted in their application. A more promising approach is likely to be through a study of the thermodynamic properties of the systems stone–water and stone–binder. Suggestions have been made that the heat of wetting might provide a useful index of the adhesivity of binders to stones,[13,38] and in fact a preliminary study of the problems involved is in progress at the Road Research Laboratory. The heat of immersion or wetting of a solid in a liquid is a direct measure of the energy liberated in forming the adhesive bond between the solid and the liquid. In general, with most mineral solids the heat of wetting by water is much larger than that with any non-polar organic liquid, particularly with a hydrocarbon oil. This type of approach is complementary to that of studying the degree of adsorption of binders on stones, and together the two approaches may lead eventually to a basic understanding of the processes of wetting and adhesion in bituminous materials and to the mode of action of additives which are already known to improve resistance to water.

ADHESION TESTS

It is clearly desirable that there should be a reliable method of determining in the laboratory whether or not a bituminous binder will adhere well to an aggregate in the presence of water. Since the studies of physico-chemical properties of the system binder–stone–water have so far not proved sufficiently conclusive to lead to the development of a reliable method for the routine testing of bituminous materials which is based on measurements of the fundamental properties of the system, it has been necessary to develop arbitrary tests which may be used to examine the various combinations of roadstones and binders used in bituminous road construction.

Numerous tests have been described, most of which fall into one of six basic types. In five of these a sample of aggregate (sometimes graded, sometimes single-sized) is coated with a bituminous binder and then immersed in water under controlled conditions. The degree of stripping of binder from the aggregate after a known period of time is measured. The various techniques differ in the type of specimen used in the test, the conditions under which the sample is immersed in water, and the method by which the degree of stripping is assessed. The sixth type of test is rather different in principle in that an attempt is made to coat stone with binder in the presence of water; in this case the degree of coating obtained is used as the index of adhesivity.

These six types of test are:

(1) Static immersion tests.
(2) Dynamic immersion tests.
(3) Chemical immersion tests.
(4) Immersion mechanical tests.
(5) Immersion trafficking tests.
(6) Coating tests.

There are several examples of each of these types of test, but in most cases the individual tests of one type differ in detail rather than in principle.

Static Immersion Tests

In this type of test the coated aggregate is immersed in water and the degree of stripping of binder from the aggregate is estimated. Most tests of this type employ a visual assessment of the stripping, for examples see Lee,[2] and Mallison and Schmidt,[39] and this has

been shown to lead to poor reproducibility.[40,41] An alternative method of assessment is to measure the quantity of light reflected from the sample before and after immersion in water by means of a photo-electric cell.[42] Yet another approach towards the elimination of visual assessment has been provided by the use of a radioactive calcium salt which is coated over the surface of the aggregate before the binder is applied and is then able to dissolve in water when stripping has occurred.[43] This method is fundamentally unsound, since the interface which is studied is no longer binder and stone but instead binder and calcium salt. It is known that small amounts of materials such as calcium salts may sometimes have a marked effect on the stripping of binders from the aggregate when studied by a static immersion test.

Dynamic Immersion Tests

This type of test is similar in general principle to that described above, but the sample is agitated mechanically by shaking[44-46] or kneading.[32] The Nicholson wash test[44] is typical of several dynamic immersion tests. The method of assessing the degree of stripping in such tests may involve visual estimation, which is usually unsatisfactory (see above), or determination of the quantity of uncoated aggregate which separates from the original sample.

Chemical Immersion Tests

The best-known example of this type of test is that described by Riedel and Weber,[47] but others of similar type also exist. Roberti[48] found that when mineral matter impregnated with bitumen was boiled in an aqueous solution of certain inorganic salts the bitumen tended to separate from the mineral solid. Riedel and Weber applied this principle to sand which was first coated with bitumen and then boiled successively in distilled water and, if necessary, in solutions of gradually increasing concentrations of sodium carbonate (using a fresh sample of coated material with each solution). The strength of the solution of sodium carbonate in which stripping was first observed was used as a measure of adhesivity. Attempts have been made to improve this test by reducing the temperature and using larger-sized stone,[49] by measuring the amount of uncoated aggregate which separates from the coated mass,[50] and by extending the scale of the test.[51] However, the real difficulty with this type of test is that it is unsound in principle, since the subjection of the sample to such high temperatures and its exposure to the action of sodium carbonate solution bear no relation to normal road conditions.

Immersion Mechanical Tests

Immersion mechanical tests are in essence static immersion tests in which the degree of stripping of binder from the aggregate is observed indirectly by measuring the change in a specified mechanical property of a sample of bituminous material after it has been immersed in water. It is usual to employ a graded aggregate rather than single-sized stone, and this type of test may provide some information on the stability of paving mixtures under wet conditions. The mechanical properties which may be measured include shear strength,[50,52,53] tensile strength,[54-56] flexural strength,[54] compressive strength.[54,57-60] penetration of a cone,[61] and resistance to abrasion.[62] One major criticism which may be levelled at most of these tests is that although much work has been carried out in the laboratory, little is known about the correlation between the tests and actual road performance of the mixtures which are tested. With some of the materials which have been examined by means of these tests, it is even doubtful whether an important practical problem really exists.

Immersion Trafficking Tests

Almost all of the tests so far discussed suffer from one major fault in that it is tacitly assumed that traffic passing over the pavement has no effect on the stripping which may occur. As has been pointed out earlier, in some circumstances traffic may play an important role in stripping. A number of tests have been described in which the bituminous sample is subjected not only to the action of water but also to stresses produced by some form of traffic. Holmes[63] has described a circular-track test, and there have been several accounts of test machines which apply traffic in the form of rolling wheels over the surface of a specimen when it is immersed in water.[13,64,65] There is good correlation in some circumstances between road behaviour of bituminous materials and the results of one immersion trafficking test.[66-67] Such tests are specially applicable to materials of the coated-macadam type, although the same principle has also been applied to the study of surface dressings.[32] Where it can be shown that traffic plays an important part in the stripping process, it is rational that an immersion trafficking test should be employed. At present no published information is available on the reproducibility of such tests, and further evidence is desirable to demonstrate more completely the correlation between the results of such tests and road performance.

Coating Tests

In these tests, an attempt is made to obtain adhesion between an aggregate and a binder when water is also present. The test may take the form of a mixing test as, for example, in the water–asphalt preferential test[68] or alternatively a plate or tray test which is especially applicable to the study of surface dressing materials, as exemplified by the immersion

tray test.[69] This test, which was developed from the plate test described by Lee,[2] is very simple and involves the immersion of a tray of binder in water and then the application of chippings to the surface of the binder. No adhesion is obtained under these conditions with normal roadstones and binders, but the test is extremely convenient for examining how surface-active agents improve adhesion between binders and aggregates for use in surface dressing under wet conditions.

EFFECT OF ADDITIVES ON ADHESION

Although it has been advocated that polar materials, such as organic acids or alcohols, should be added to bitumen to improve its adhesivity, the improvement effected by such additions rarely seems to have been adequate.[63, 70–72] However, it has been found that the addition of up to 10 per cent of road tar (a source of organic acids) to bitumen may improve adhesion in coated-macadam wearing courses, although even in this case stripping is not entirely prevented.[65,73,74] Again it has been suggested that aggregates heated in a dryer with incomplete combustion have improved adhesive properties due to the deposition of a layer of oil or soot on the surface of the stone.[75, 76]

Special fillers, such as hydrated lime [77] or Portland cement,[78] have long been used to improve adhesion in bituminous materials, especially in pre-mixed materials. These fillers are particularly valuable when it is desired to coat cold and wet aggregates.[79, 80] It has been claimed that fly-ash has an important beneficial effect on adhesion,[81] but other work has cast doubt on this assertion.[82] The use of fillers such as hydrated lime reduces stripping in coated macadam to an insignificant level.[83] It is usually assumed that the filler reacts with the organic acids present in all bituminous binders to form surface-active calcium salts such as calcium naphthenate or calcium phenate. In some cases, it is desirable to add additional acids to a binder to ensure adequate adhesion,[83] but the precise type of acid which gives the best result, and the optimum quantity, are not yet established conclusively. Although the above explanation of the effect of hydrated lime in a bituminous mixture is an attractive hypothesis, very little direct experimental evidence is available to confirm it. In particular, two facts remain unexplained: it is known that calcium salts when added to bitumen do not improve adhesion in the same degree as hydrated lime,[73] and also that a limestone filler does not behave in the same way as hydrated lime and in fact appears to have little influence on the adhesion of binders to aggregates.[17]

For many years, attempts have been made to improve adhesion in bituminous materials by adding surface-active chemicals to the binder. It has been claimed that some soaps of suitable metals (calcium, lead, iron) may improve adhesion.[84] The effect of such soaps is largely to reduce the interfacial tension between binder and water and, although this may cause a slight improvement in resistance to stripping, it is rarely adequate in practice.[16, 73]

A more promising approach is to employ additives which show cationic surface-activity. These materials tend to be strongly adsorbed at the stone/binder interface, and thereby reinforce the adhesive bond and render it resistant to water. The first compounds of this type to be studied extensively were quaternary compounds, of which cetyl pyridinium bromide [16] and cetyl trimethyl ammonium bromide [13] are examples. Cetyl pyridinium bromide showed considerable promise in laboratory tests, but when used in surface-dressing trials it did not come up to expectations. It was believed that the reason for this behaviour was that an insufficient quantity of the agent had been added to the binder and it was felt that a more efficient technique was desirable which would be more economical in its use of the agent. Alternative methods, in which the agent was applied directly to the interface, were therefore developed.[13] It has also been found that quaternary compounds caused little improvement in the adhesion of pre-mixed materials when added to the binder in concentrations of up to 1 per cent.[83]

Subsequently, more powerful agents, usually organic amines of relatively high molecular weight, have been investigated. The use of amines to prevent stripping has been shown to be effective in surface dressing [85, 86] and is now general practice in Sweden [87] and in some parts of Great Britain.[88] Recommendations on the use of adhesion agents for the prevention of wet-weather damage to surface dressing have been published in Great Britain.[89] There is some evidence that amines may also be used to prevent stripping in pre-mixed bituminous materials; [90] at present the minimum quantity required is not clearly established.

Although the addition of an agent to the binder is exceptionally convenient, it has certain disadvantages. The quantity of agent required depends very much on the type of binder and type of aggregate used,[89] and in some conditions the extra cost involved may not be economically justifiable. However, against this extra cost must be balanced savings achieved from the more efficient use of plant and labour when delays caused by wet weather are eliminated.[86, 88] So far no cationic agent has been found which is both effective in improving adhesion and also stable towards heat when dispersed in a bituminous binder. The activity of an agent falls off at a rate which depends on the time of contact with the hot binder and the temperature at which the binder is maintained.[69, 83, 91] This effect appears to be caused by a chemical reaction between the agent and active constituents, probably acids, in the binder. For this reason, it is advisable

to reduce as far as possible the period of time during which a mixture of agent and binder is maintained at an elevated temperature and, in particular for surface dressing, the best procedure is to mix the agent and binder just before they are to be used.[83, 92]

It has been shown that the addition of some surface-active agents may cause a change in the viscosity of a bituminous binder, but for many practical applications this is not of great importance.[89, 93, 94]

Other materials which have been proposed as additives to bituminous mixtures to improve their adhesion include furfural,[95] sulphonated oils,[96] and silicones.[97] None of these treatments has achieved widespread success in practice.

There have been claims that the addition of rubber to bitumen may improve its adhesive properties,[98] but the evidence for this claim is extremely doubtful, and in fact there is slight evidence that the adhesivity of rubber–bitumen may be similar to or even poorer than that of a normal bitumen.[99–101]

ASPECTS REQUIRING FURTHER STUDY

In spite of the considerable amount of accumulated knowledge on adhesion in bituminous road materials there are several aspects on which more information is required to complete our understanding of the subject. It is desirable that more should be known about "dry adhesion." With the trend towards more viscous binders, which has been caused by modern traffic requirements, the practical problem of the relation between wetting of stone and the viscosity of a bituminous binder is of great importance, particularly in surface dressing. Possibly the method described by Leroux,[102] in which he attempted to measure a "wetting temperature," may provide an approach to this problem. Again, little is known at present about the changes with time in the strength of the bond between stone and a bituminous binder, especially when the binder has weathered. One of the most promising approaches so far developed towards the measurement of the strength of the bond between a binder and a stone is that of Ariano,[56] which might be applicable in this case.

Relatively few accounts have been published of the types of failure of bituminous materials caused by water. The mechanisms of stripping and subsequent failure of coated materials, including macadam, fine cold asphalt, and even hot asphalts of the asphaltic concrete type, require much more study. Although traffic appears to play an important part in the stripping of wearing-course materials, this factor may be of less importance in base-course materials. It is regrettable that so little is known at present about the stripping which is liable to occur in base-course materials.

Although the major problems in the prevention of wet-weather damage to surface dressings have now been largely solved, clarification is required on a few points. It is known that the addition of an adhesion agent to a bituminous binder may influence the viscosity of the binder:[93, 94] recent experience has suggested that although for many purposes this change in viscosity may be neglected, in some instances it may be of practical significance; the available data on this point are not sufficient to predict with certainty how large a change in the viscosity is likely in any specific instance. The amount of an adhesion agent required to promote good adhesion under wet conditions may depend not only on the chemical type of the binder and on the nature of the aggregate but also on the viscosity of the binder and the temperature of the road surface.[103] Work is in progress on this subject at the Road Research Laboratory.

Some problems concerned with the prevention of stripping in coated materials remain. The requirements with respect to the acidity of bitumen when used with fillers such as hydrated lime have yet to be fully defined and the mechanism of this process for the improvement of adhesion in coated materials is at present not properly understood. So far, general recommendations for the use of surface-active agents to prevent stripping in coated materials have not yet been produced, although work now in progress at the Road Research Laboratory should satisfy this need. However, so long as the available adhesion agents show their present sensitivity towards heat when dispersed in bituminous binders, there will always be technical difficulties in their use. The ultimate aim of all work to produce new agents for use with bitumen or tar must be the development of an agent which shows both high efficiency at low concentrations in the binder and at the same time high stability towards heat when the mixture of binder and agent is maintained for long periods of time in the range of temperatures from 100° to 150° C. Several recent papers have shown that considerable attention is being paid to this problem, and new agents are now appearing which are claimed to be more heat-stable than earlier types.[104–107] No agent so far tested at the Road Research Laboratory has, however, shown both adequate activity and heat stability.

The results of the physico-chemical studies of the water–stone–binder system have not been very satisfactory in providing a basic understanding of the problems of adhesion in bituminous materials. It is possible that a new approach designed to obtain basic thermodynamic data on the system may lead to a clearer picture.[108] Since both the formation and the development of the adhesive bond depend very much on adsorptive forces, a more detailed study of the processes of adsorption in bituminous materials

may prove rewarding, especially in relation to the full explanation of the effects of surface-active agents on adhesion under wet conditions.

Further investigation is required of a number of adhesion tests and especially some of those recommended for study by the Technical Committee of the Permanent International Association of Road Congresses.[109] Until more is known about these tests it is difficult to assess their relative merits as methods of studying problems of adhesion. In particular, more information is required on the correlation between the results of adhesion tests and the behaviour of bituminous materials under road conditions. Studies are also required of the reproducibility of all types of adhesion test which may be considered for standardization.

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THE DENSITIES OF LIQUID C_3 AND C_4 ALKENES AT TEMPERATURES ABOVE THEIR BOILING POINTS *

By D. W. MORECROFT †

SUMMARY

The liquid densities, under their own vapour pressures, of propene, *iso*butene, butene-1, *cis*-butene-2, and *trans*-butene-2 have been measured over the temperature range 0° to 80° C.

DURING a recent investigation it was required to know the densities of C_3 and C_4 alkenes over the temperature range 0° to 80° C. As published information does not cover this range the densities had to be measured.

Because of the pressures developed by the hydrocarbons over this temperature range, conventional methods of determining densities could not be used. A special method was therefore devised in which a density bomb was used. This bomb, of capacity about 100 ml and weight 2 kg, with a maximum safe working pressure of 800 lb/sq. in. was made in stainless steel (Fig 1). To ensure that the bomb was always full of liquid, and to prevent a build-up of hydrostatic pressure when the liquid contained in it expanded on heating, a removable " expansion bomb " was fitted to the top of the density bomb. As a further precaution against explosion of the assembly, a bursting disk was fitted to the density bomb, and during the density determinations frequent observations were made of a pressure gauge fitted to the expansion bomb.

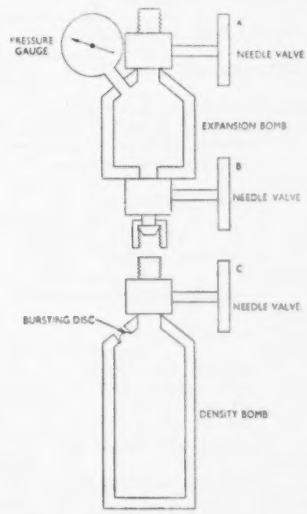

FIG 1

APPARATUS FOR DETERMINING DENSITY OF LIQUIDS ABOVE THEIR BOILING POINTS

To avoid any change of volume through elastic deformation of the bursting disk, the bomb was before use subjected to a pressure which was just below that of the bursting value of the disk. The disk was permanently deformed into a hemispherical shape and so was not deformed by further pressure changes.

The internal volume of the bomb was determined by measuring the weights of distilled water contained by the bomb over the whole temperature range.

RESULTS

Accuracy of Results

As a test of the accuracy of the results obtained by this method, the densities of benzene were determined over the range of 15° to 80° C. The values obtained gave a linear plot of density against temperature. Values derived by interpolating from this plot are compared below with values stated by the API.

TABLE I

Comparison of Values of the Density of Benzene Obtained by the API and Thornton

Source of data	Density, g/ml		
	15·6° C	20° C	25° C
API	0·8836	0·8790	0·8737
Present work at Thornton .	0·8837	0·8793	0·8740

The API and Thornton data are in excellent agreement, and it is concluded that the method can be regarded as giving accurate values.

Densities of Alkenes

Samples of pure unsaturated C_3 and C_4 hydrocarbons used in this study have been used as reference samples in hydrocarbon chemistry. They were obtained from commercial sources and had a reported minimum purity of 99 mol per cent.

The density of propene was measured over the range 0° to 75° C.

TABLE II

Measured Densities of Propene

Temperature, ° C .	0·0	13·1	25·0	40·0	50·0	60·0	70·0	75·0
Densities, g/ml .	0·5480	0·5273	0·5064	0·4785	0·4592	0·4357	0·4034	0·3849

* MS received 5 May 1958.

† " Shell " Research Ltd.

TABLE III

Measured Densities of Butenes

(a) *Butene-1*

Temperature, ° C	0·0	14·6	25·0	40·0	50·0	60·0	70·0	80·0
Density, g/ml	0·6182	0·6012	0·5868	0·5682	0·5550	0·5431	0·5278	0·5122

(b) cis-*Butene-2*

Temperature, ° C	0·0	14·4	27·8	40·0	50·0	60·0	70·0	80·0
Density, g/ml	0·6478	0·6293	0·6137	0·5984	0·5862	0·5730	0·5598	0·5476

(c) trans-*Butene-2*

Temperature, ° C	0·0	14·5	25·0	40·0	50·0	60·0	70·0	80·0
Density, g/ml	0·6312	0·6125	0·5985	0·5803	0·5683	0·5540	0·5405	0·5283

(d) iso*Butene*

Temperature, ° C	0·0	14·5	25·0	40·0	50·0	60·0	69·7	80·0
Density, g/ml	0·6190	0·6022	0·5889	0·5696	0·5563	0·5422	0·5268	0·5107

The densities of butene-1, *cis-* and *trans*-butene-2, and *iso*butene were measured over the range 0° to 80° C.

TABLE IV

Interpolated Values of the Densities of Propene and Butene

Hydrocarbon	Density, g/ml, at		
	15° C	20° C	25° C
Propene	0·5250	0·5165	0·5065
Butene-1	0·5995	0·5935	0·5870
cis-Butene-2	0·6290	0·6225	0·6165
trans-Butene-2	0·6120	0·6055	0·5990
*iso*Butene	0·6015	0·5950	0·5890

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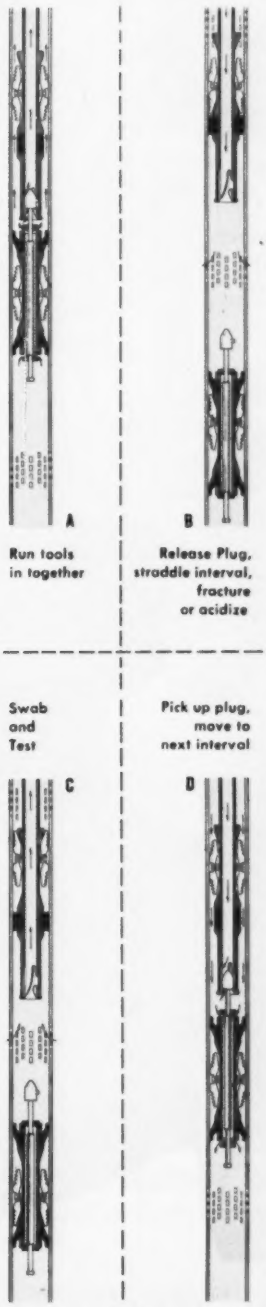

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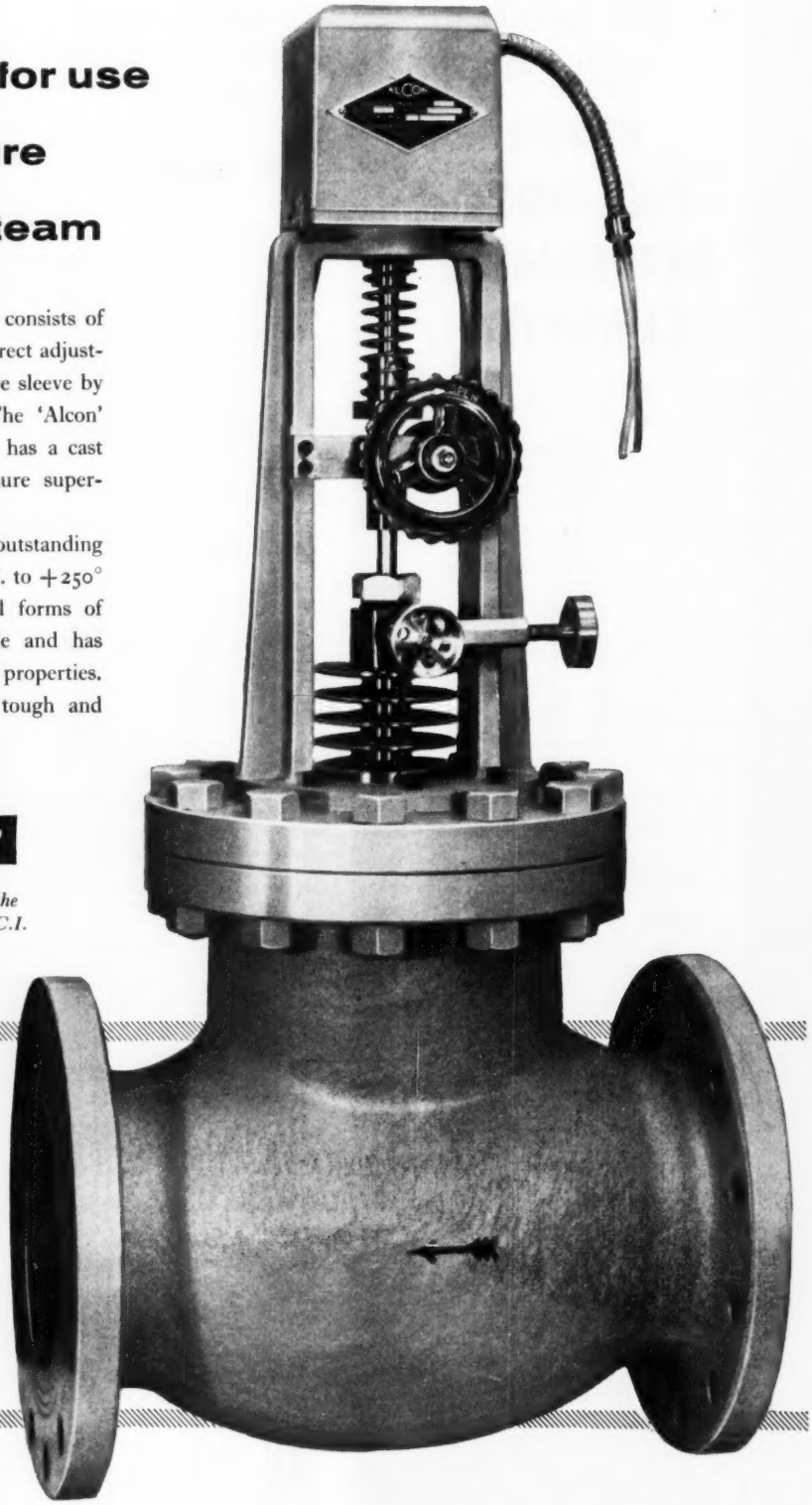

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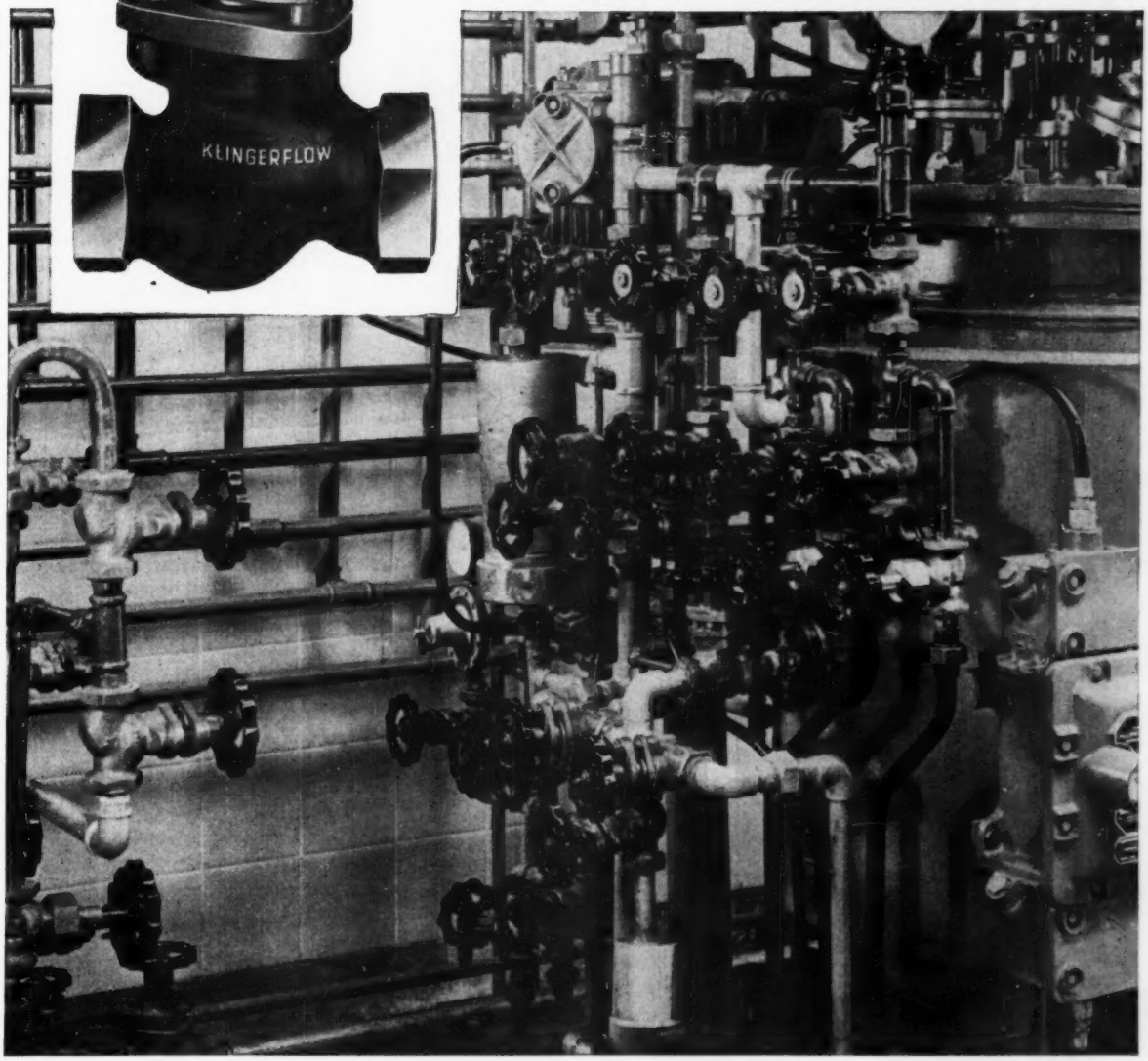

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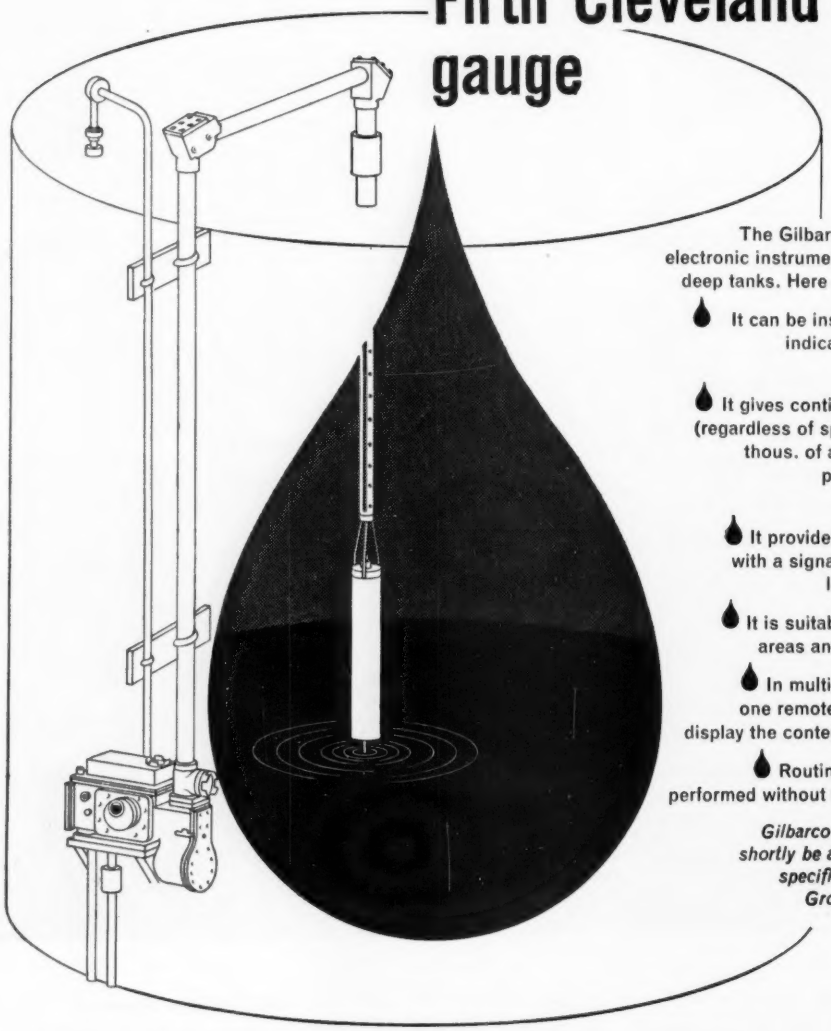

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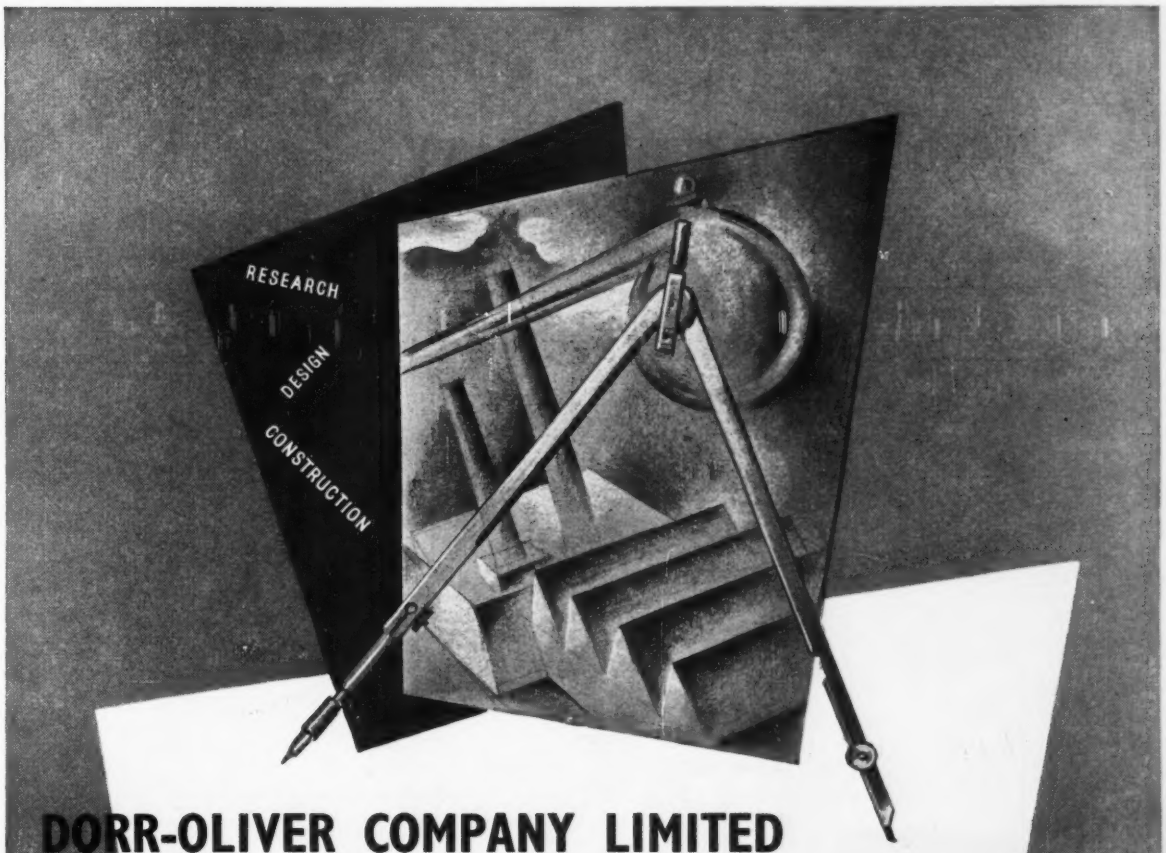

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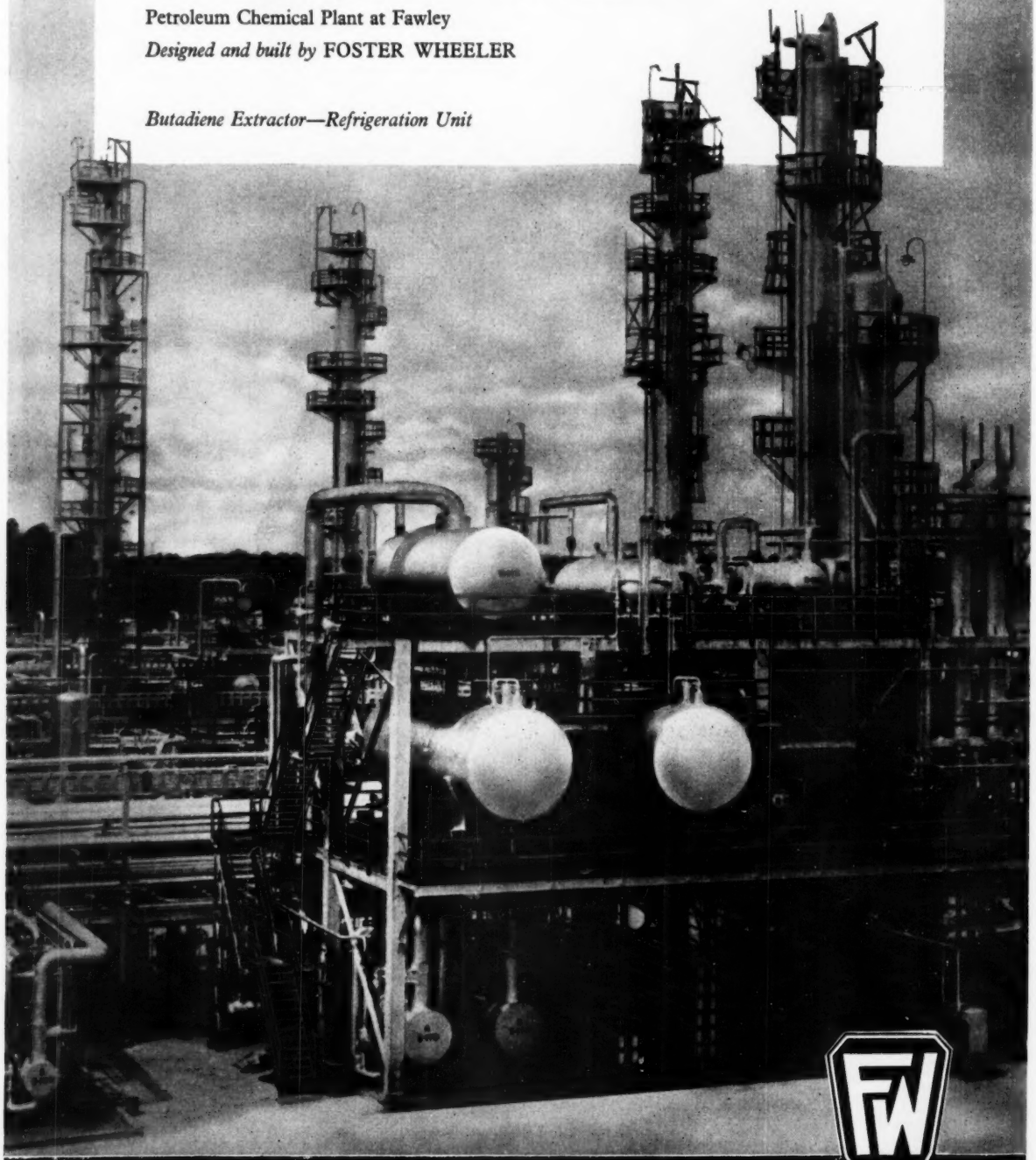

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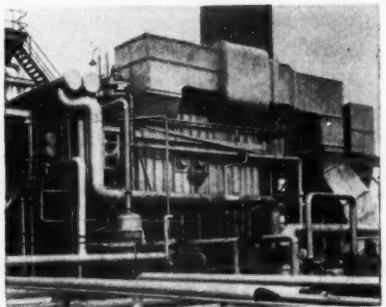

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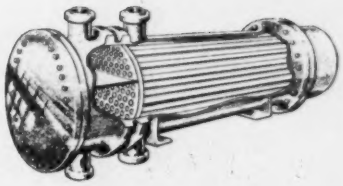

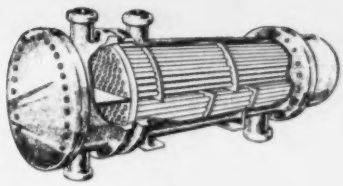

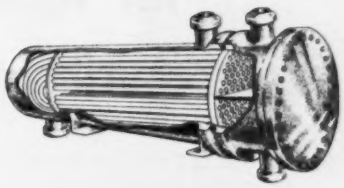

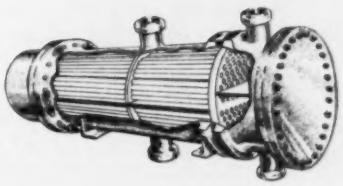

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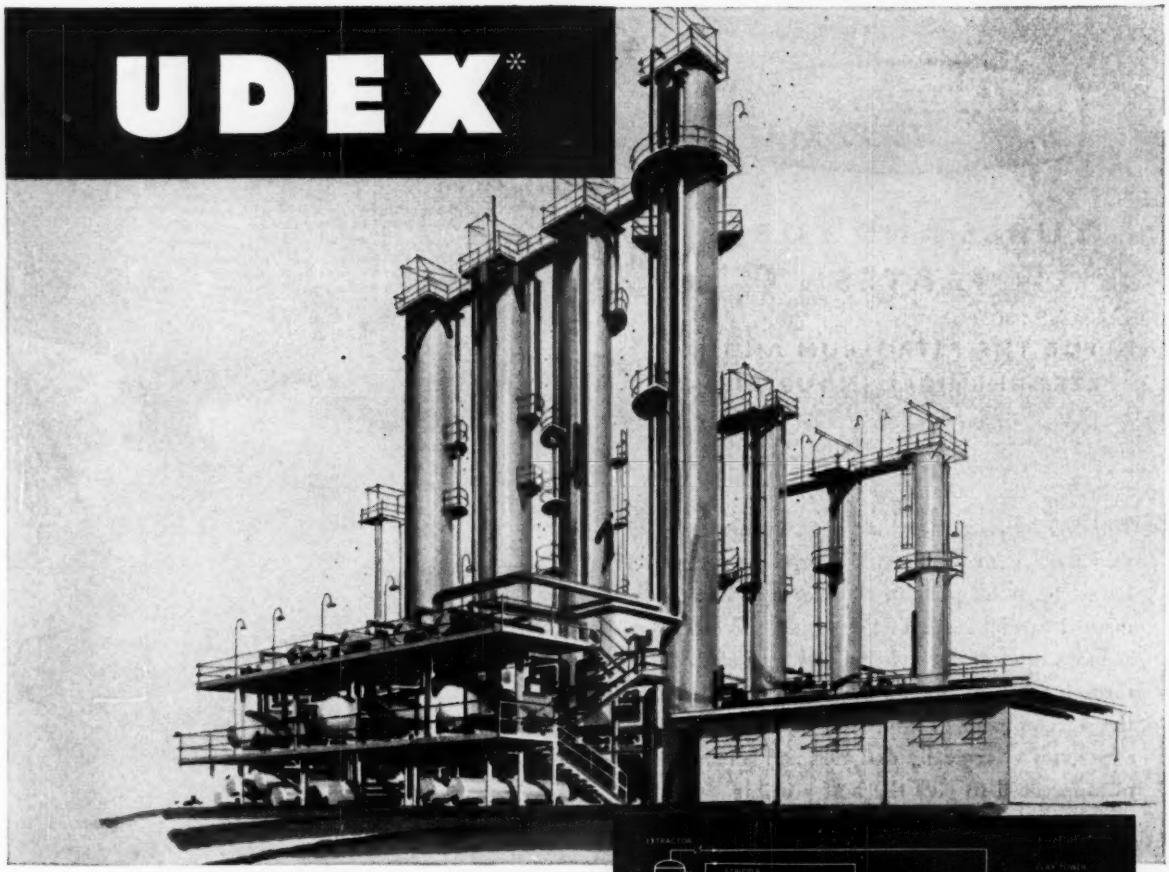

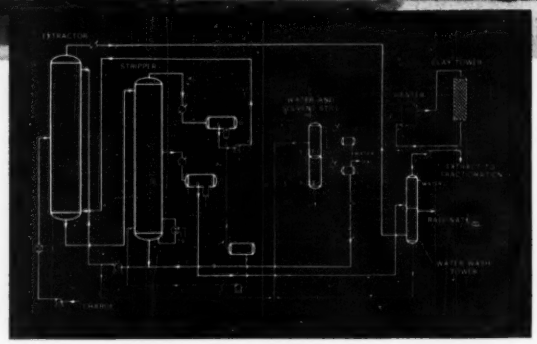

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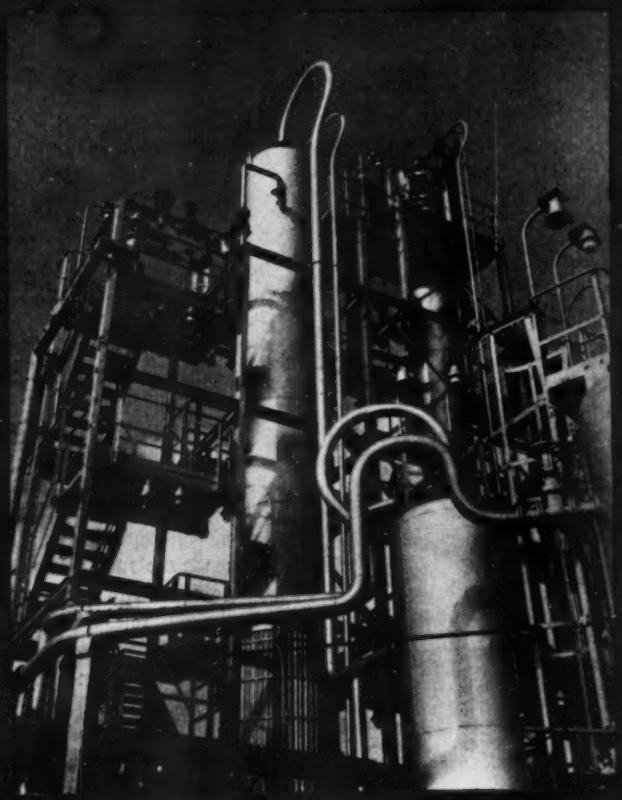

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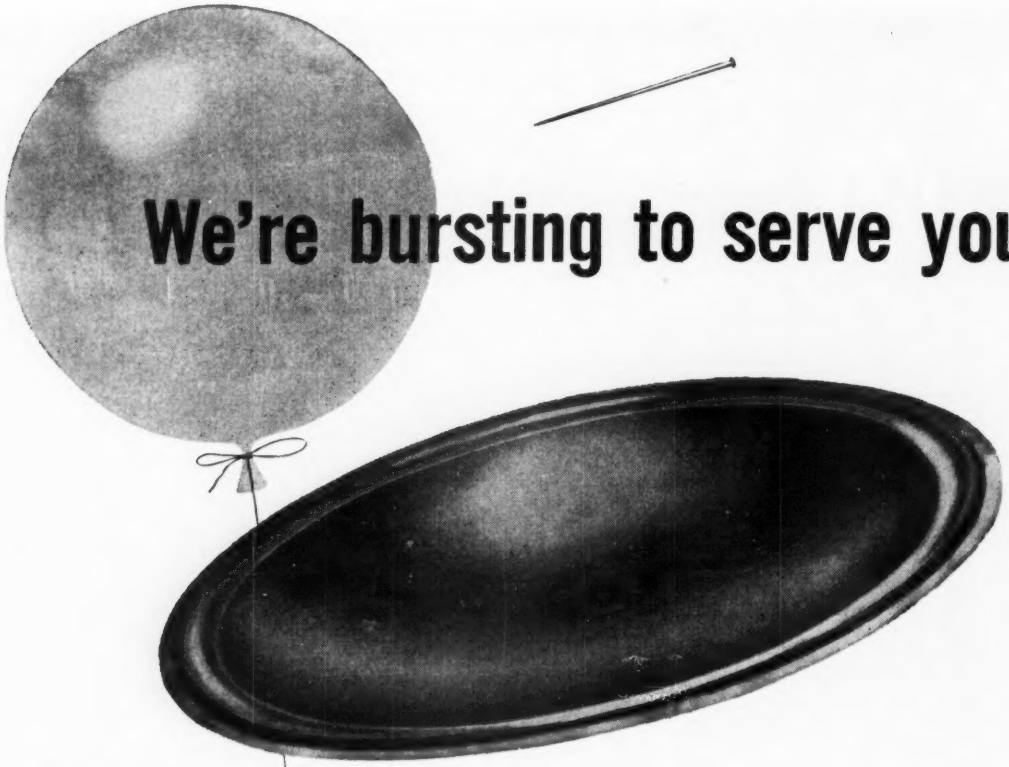

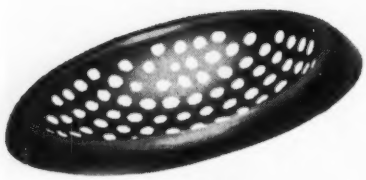

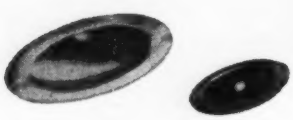

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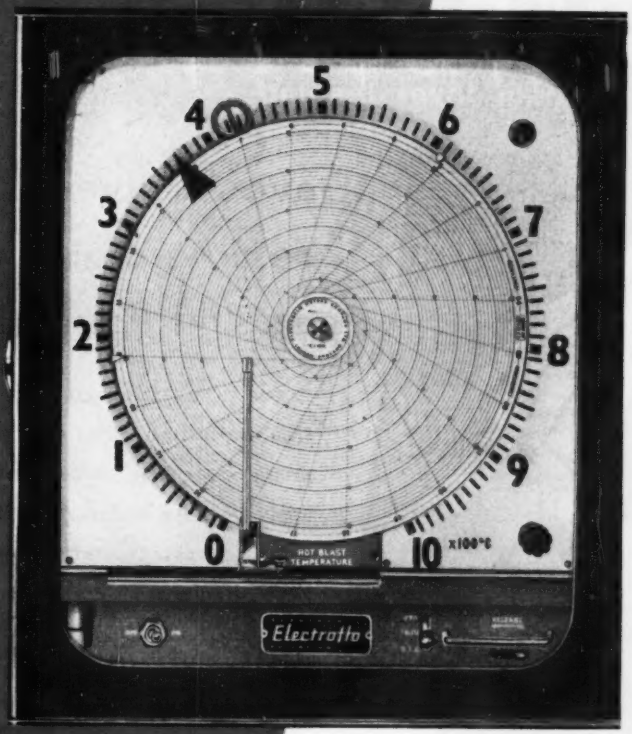

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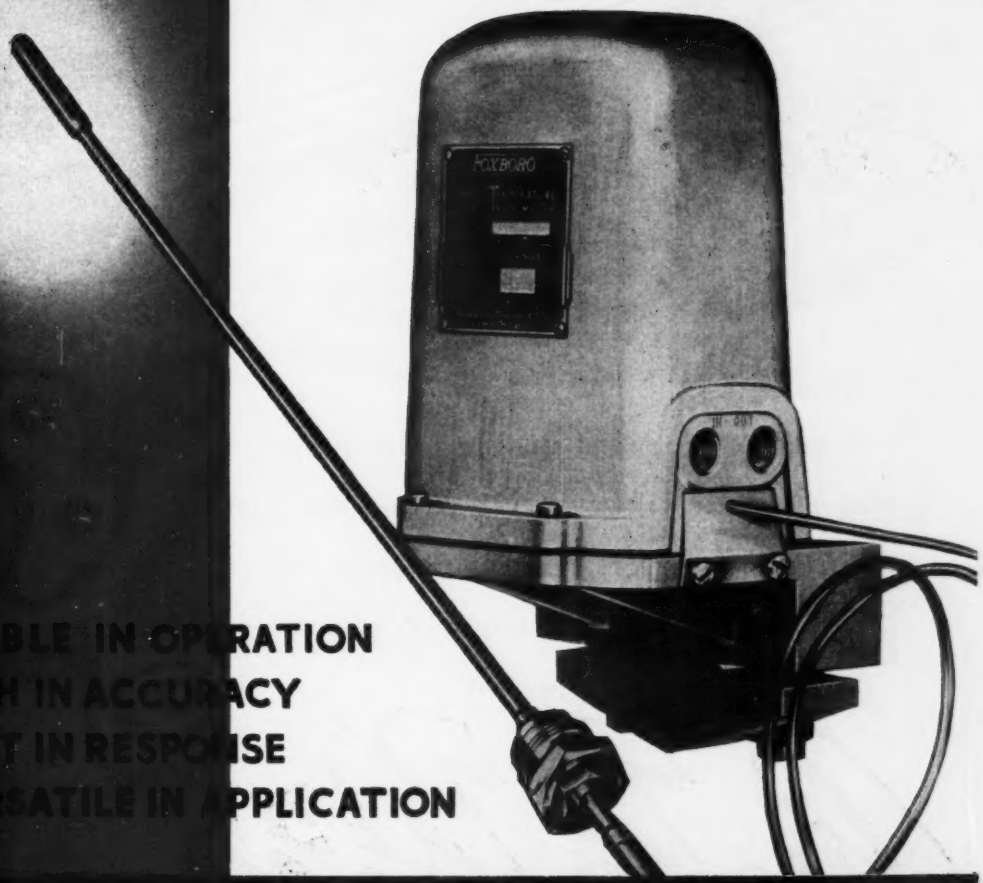

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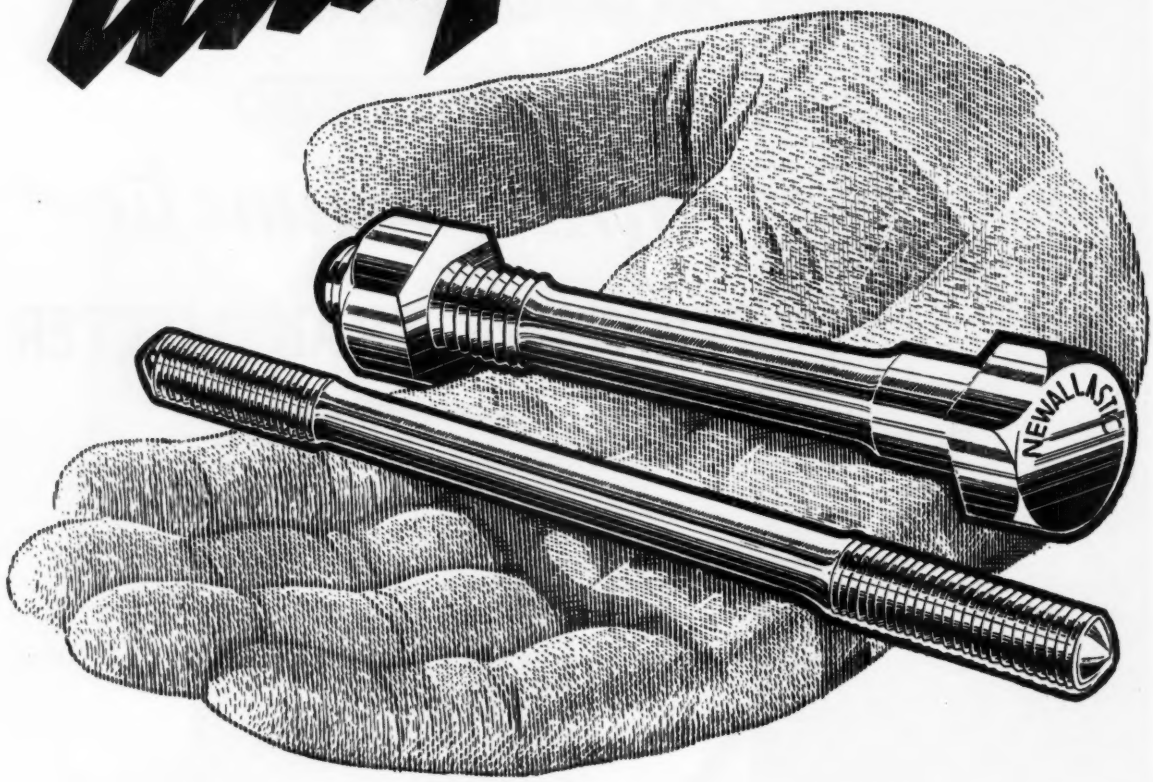

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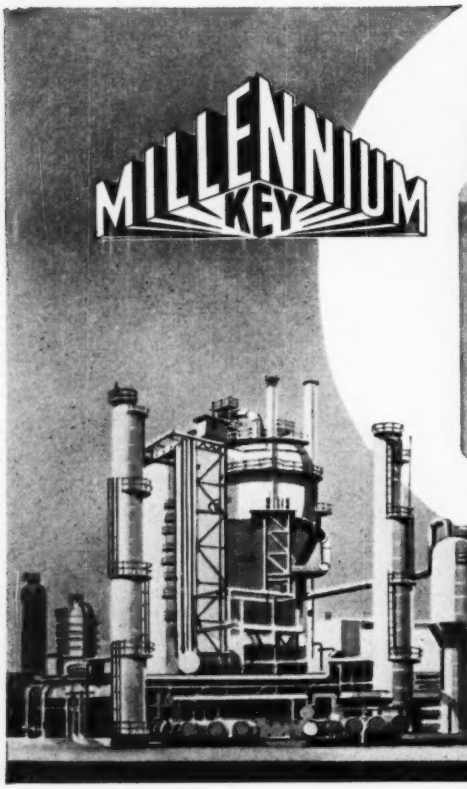

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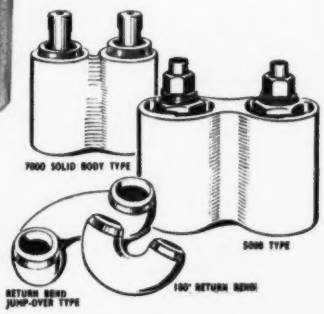

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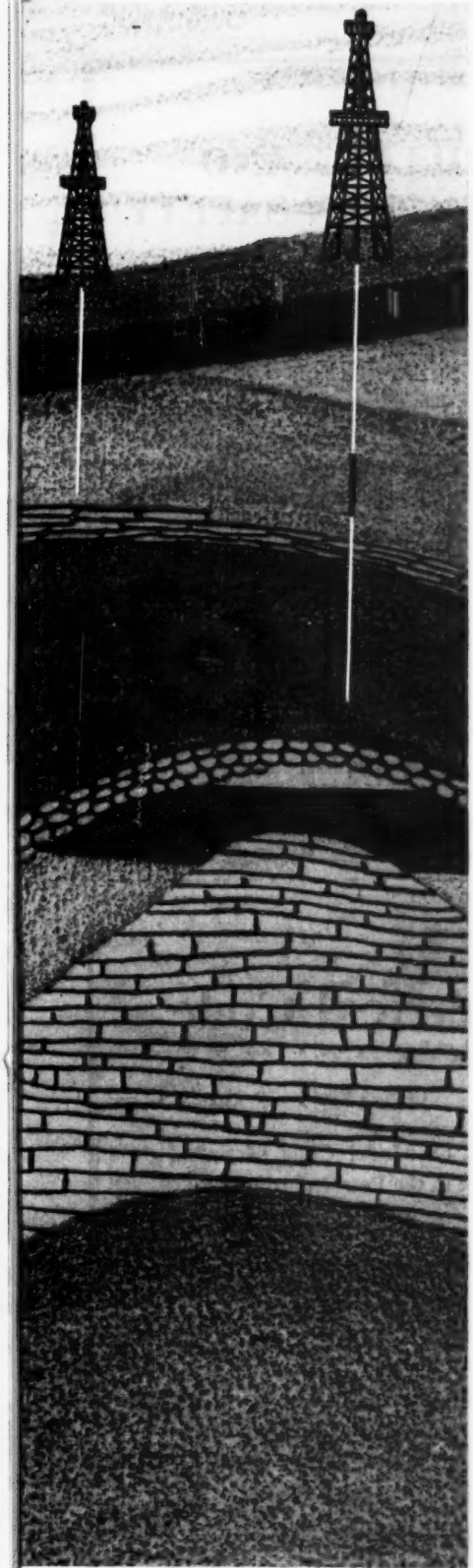

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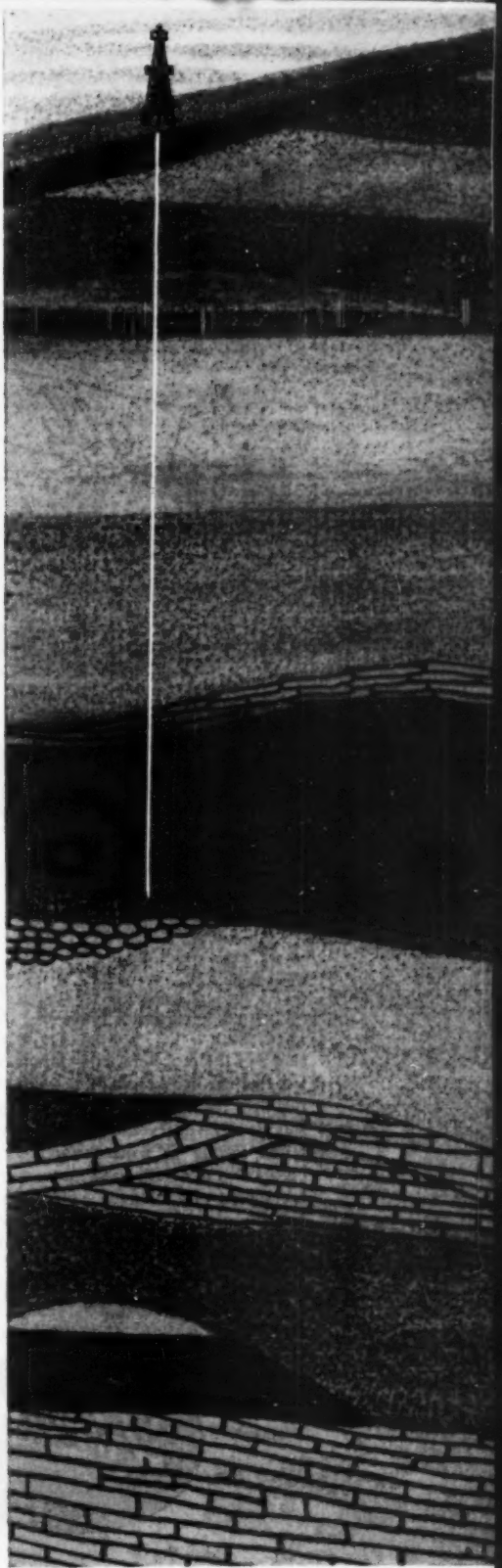

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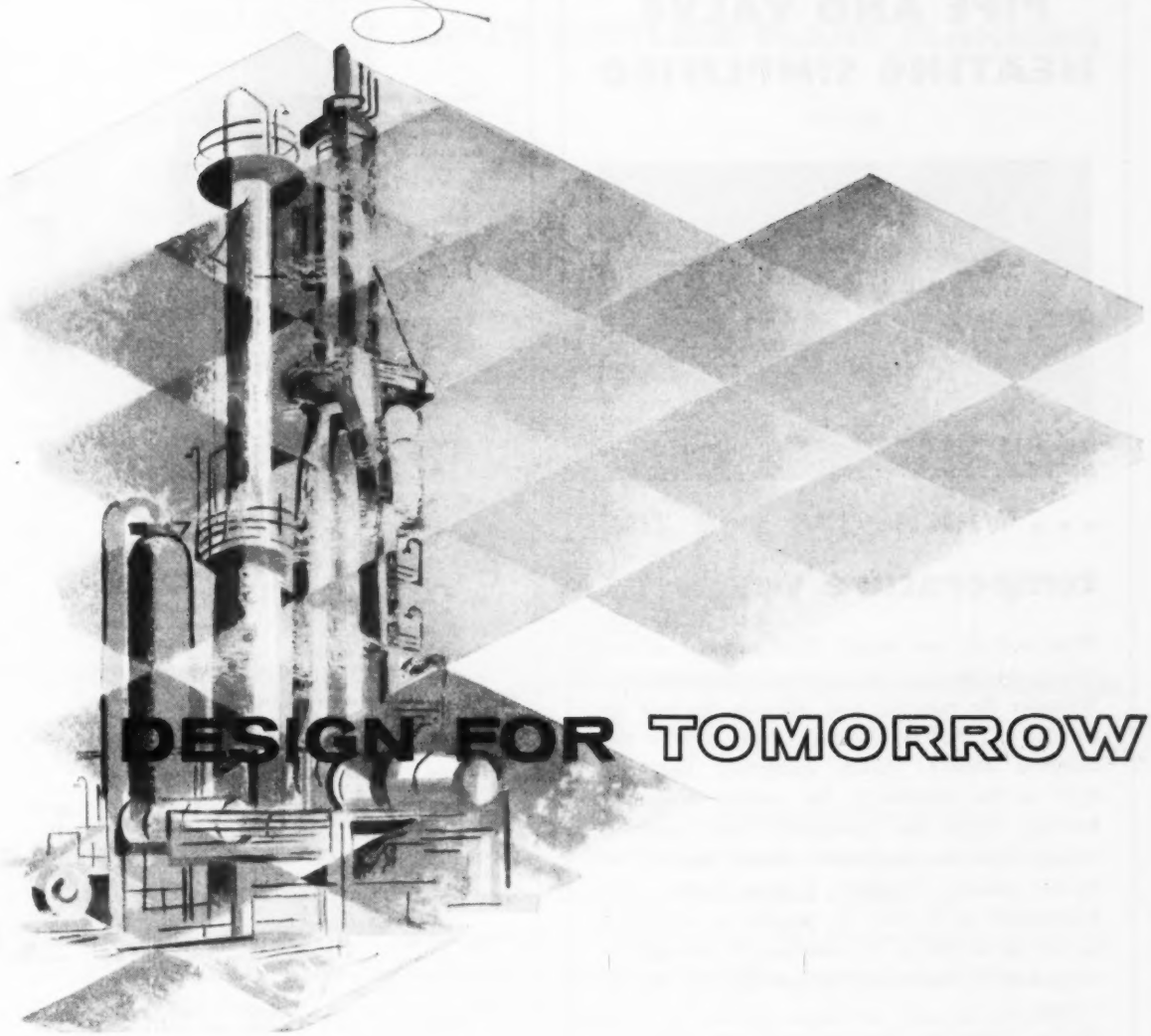

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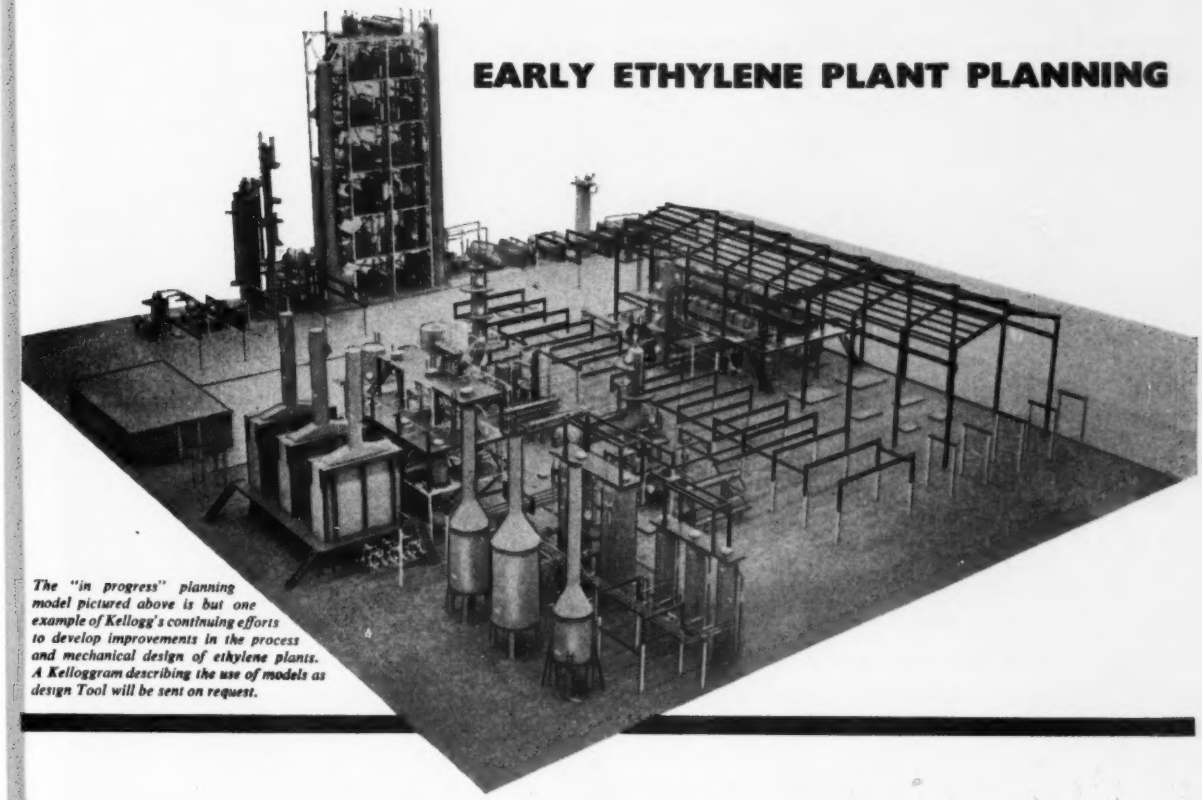

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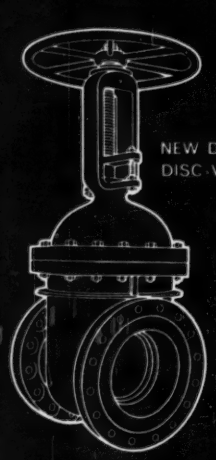

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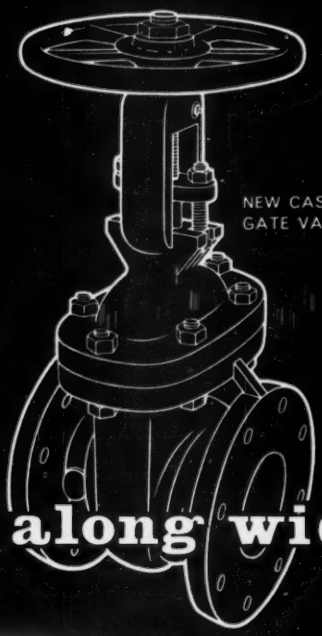

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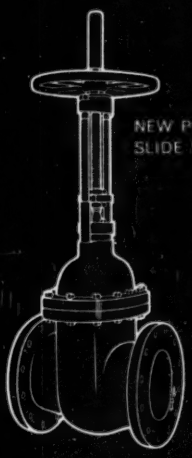

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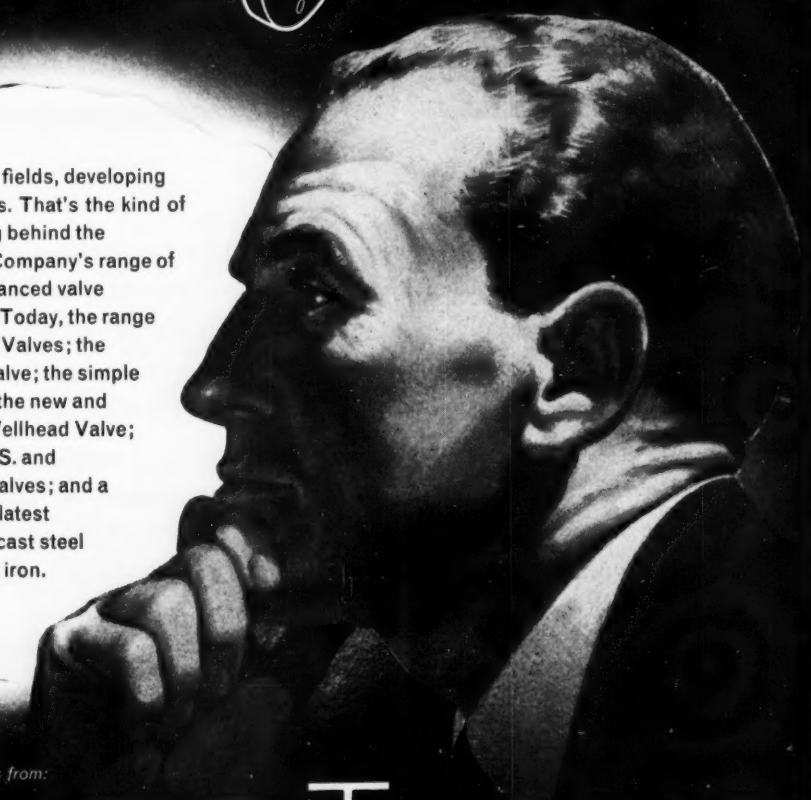

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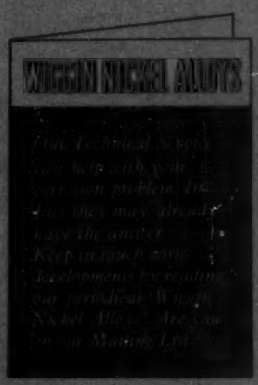

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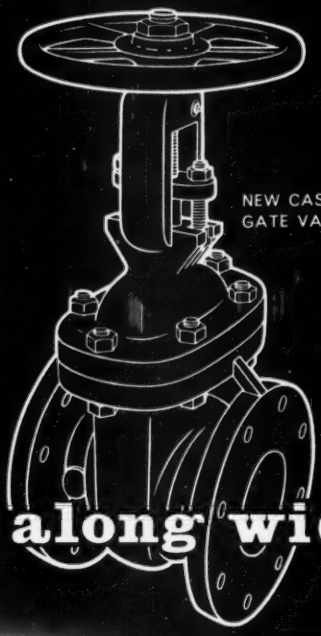

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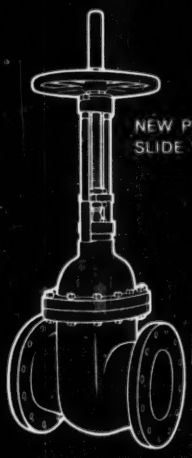

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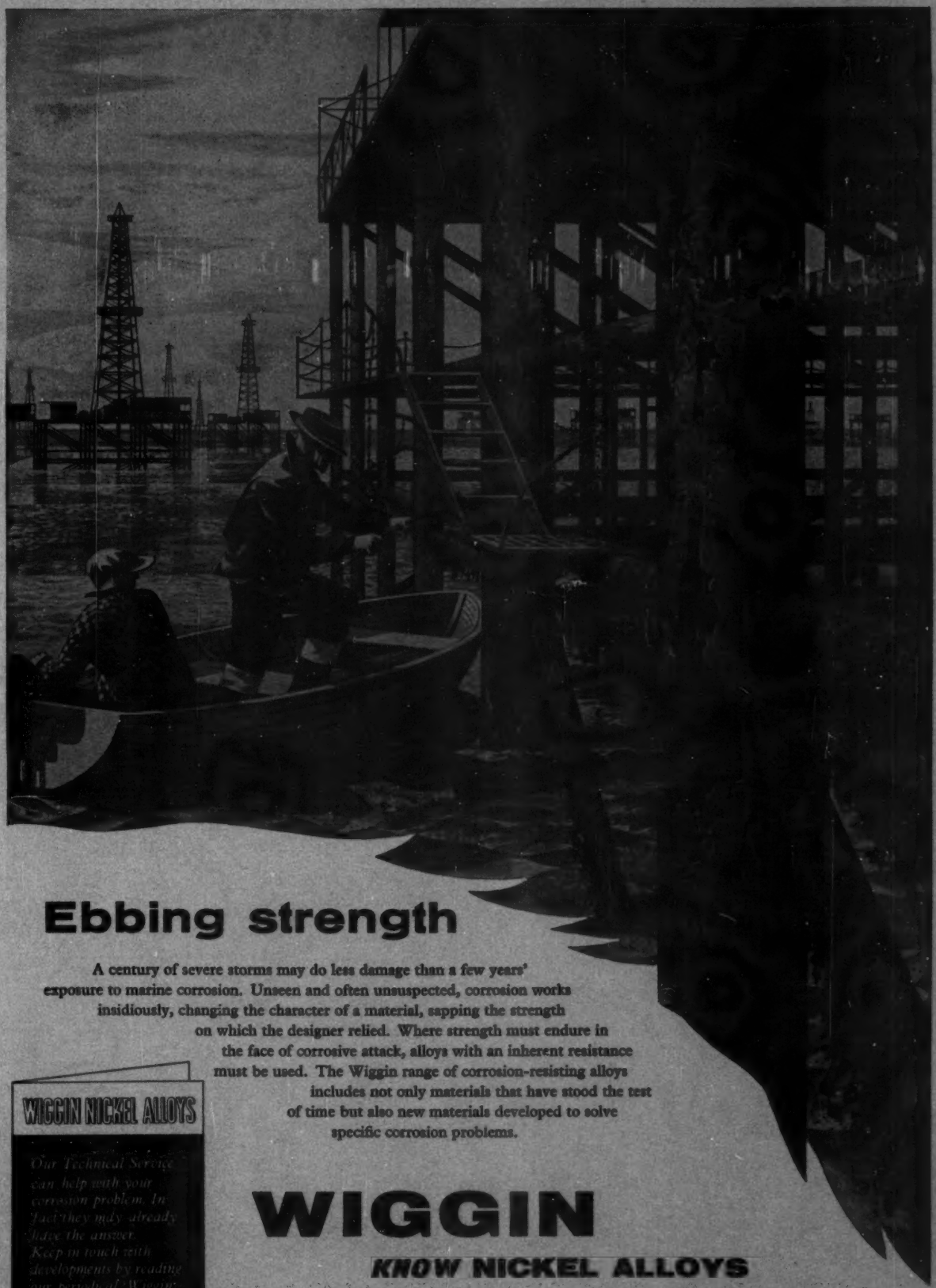

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